ANNUAL TECHNICAL REPORT
MATERIAL

July 1,

(11) 3⊄ Jw: 84

(6)

ANNUAL TECHNICAL REPORT,

MATERIALS RESEARCH LABORATORY

JULY 1, 1979 - JUNE 30, 1980.

Brown University

Providence, Rhode Island 02912

(12) 172
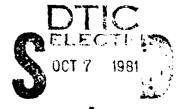
(15) √NSF-

A Report on Grant No. DMR76-80560 A01 *new*

with the

National Science Foundation

Washington, DC 20550

DTIC
ELECT
OCT 7   1981

A

411291 Gw

Sources of Support for the Research Described in this Report

PREFACE

The Materials Research Laboratory at Brown University is engaged in interdisciplinary research directed toward the solution of problems in various areas of Materials Science.

In this report, Sections I-IV represent major thrust areas; the remaining sections are less extensive, since they cover either new areas of activity, emerging thrusts with a smaller number of investigators, or derive their principal funding from sources other than the NSF-MRL program.

Although the research summaries in this report are contributions from individual investigators, introductions to the four major thrust area summaries have been provided by investigators who during the reporting period assumed the functions of coordinators of those thrust areas. These are: Microscopic and Macroscopic Dynamic Plasticity, R. J. Clifton; Fracture of Solids, J. R. Rice; Inorganic Glasses, W. M. Risen, Jr., and Chemisorption and Related Surface Interactions, P. J. Estrup.

Since many of the research areas are interrelated, cross references have been made when the work might with equal justice have been placed in two or more sections.

The largest single source of support of this Laboratory is the Materials Science Branch of the National Science Foundation. Substantial support also came from sixteen other agencies and, of course, Brown University.

The Materials Research Laboratory at Brown University is administered technically by a Director, Associate Director, and a committee composed of faculty members in representative areas of Materials Science.

The present appointees are:

Director:	G. S. Heller
Associate Director:	C. Elbaum
Advisory Committee:	R. H. Cole
	L. N Cooper
	P. J. Estrup
	J. R. Rice
	J. Tauc

Table of Contents

SECTION 1

Microscopic and Macroscopic Dynamic Plasticity

Introduction

Research in this area is directed toward development of sufficient understanding of the mechanisms of plastic deformation to be able to formulate constitutive relations that model plastic deformation of single crystals and, ultimately, structural metals. Both analytical and experimental investigations are being conducted. The size scale on which mechanisms are examined varies from the atomistic level in quantum rate theory calculations, through the microstructural level in dislocation mobility studies in single crystals, to the macroscopic scale of plastic deformation of polycrystals.

Re-examination of the analysis of the decay of the elastic precursor in plate impact experiments on single crystals has drawn attention to the possible importance, and even dominance, of the effects of surface damage. A critical experiment to examine this possibility is being developed. In other work on dislocation mobility in single crystals, a technique is being developed for determining the attenuation and the change in elastic wave speed of ultrasonic waves during and immediately following plastic deformation caused by a relatively large amplitude stress pulse.

The relationship between strain rate, stress, and temperature has been examined for bcc metals. Interesting strain rate history effects have been obtained at low temperatures ($\sim$-190°C) for a hot-rolled steel. Possible models for strain-rate history effects and temperature history effects have been considered.

On the atomistic level, quantum rate theory has been extended to the case of an asymmetric double-well potential. In addition, the form of the elastic moduli of centro-symmetric crystals has been derived in terms of the electron density and its distortion due to the crystal deformation. Conditions for the moduli to satisfy the Cauchy relations have been established.

Other investigations have been directed toward understanding dynamic plastic deformation at higher strain rates, under non-homogeneous deformations, and for non-proportional loading paths. Pressure-shear plate impact experiments on thin specimens of commercially pure aluminum sandwiched between hard elastic plates have shown a marked increase in flow stress between strain rates of $10^3 s^{-1}$ and $2 \times 10^5 s^{-1}$. This increase in flow stress suggests a change in the rate controlling mechanism for plastic deformation at these exceptionally high strain rates. The stability of homogeneous plastic deformation at high strain rates where inertia effects are significant has been examined. Explicit results have been obtained for several limiting cases. Finally, the effects of non-proportional loading paths have been examined by an analysis of plastic waves of two-dimensional anti-plane strain and by pressure-shear impact experiments on α -titanium plates. Comparison of calculated final strains for a smooth yield surface model and a corner theory model indicates little difference in the calculated final states of anti-plane strain. Velocity-time profiles for the α -titanium plates indicate that the effects of strain-rate sensitivity as well as non-proportional loading paths will have to be included before the material's dynamic plastic response can be modeled satisfactorily.

SECTION 1

Microscopic and Macroscopic Dynamic Plasticity

Individual Contributions

Mechanics of Dislocations in Single Crystals

The decay of the elastic precursor has been re-examined from the viewpoint of the elastodynamics of dislocations. Solutions for long straight dislocations set in motion by an incident plane wave have been used to derive the rate of decay of the elastic precursor. The resulting equation for precursor decay is essentially the same as the commonly used one, which is based on an elastic/visco-plastic model of the crystal. The only difference is a small correction due to the fact that for the elastic/visco-plastic model dislocations of opposite sign moving in opposite directions have the same effect on precursor decay, whereas according to the elastodynamics analysis, dislocations propagating toward the wavefront have a greater effect than those propagating away from the wavefront. Based on this confirmation of the validity of the precursor decay relation, an explanation for the larger-than-predicted decay observed in experiments has been sought in terms of possible errors in either the dislocation velocity or dislocation density that appear in the precursor decay relation. Analytical and experimental evidence suggests that usual estimates for dislocation velocity are reasonable, but that large errors in estimates for dislocation density occur at the impact face. Surface damage during specimen preparation, and the impact of rough surfaces, are responsible for dislocation densities at the surface that are several orders of magnitude larger than in the interior of the crystal. The large dislocation densities near the impact face are believed to be responsible for much of the larger-than-predicted reduction in precursor amplitude. The decrease in precursor amplitude with increasing distance of propagation appears to be compatible with dislocation densities at the wavefront once the nonlinear elasticity effects of unloading waves from the impact plane are taken into account. Overall, it appears that precursor decay can be explained by considering finite elasticity effects and large dislocation densities near the impact surface. In order to test the validity of this explanation, an experiment has been designed to reduce the generation of dislocations at the front and rear faces of the specimen by placing the specimen plate between two liquid layers. Preliminary experiments suggest the feasibility of conducting such critical experiments.

Principal Investigator: R. J. Clifton (Engineering).

Personnel: X. Markenscoff (Engineering), P. Kumar (Engineering), and L. Hermann (Engineering).

Publications: "The Transient Motion of a Nonuniformly Moving Dislocation," X. Markenscoff, J. of Elasticity *10* (1980), 193.

"On the Kinetics of a Frank-Read Source," P. S. Steif and R. J. Clifton, Materials Sci. and Engrg. *41* (1979), 251.

Dislocation Behavior under Stress-Pulse Loading

We have redesigned an apparatus for studying the dynamic behavior of dislocations during and immediately after the application of a short ($\sim$100 microseconds) duration stress pulse. This investigation is conducted by sampling (at 10 microsecond intervals) the attenuation and velocity changes of a high frequency ($\sim$100 to 250 MHz) ultrasonic wave, while the stress pulse is propagating through the specimen under study. The above sampling process continues for a period of several milliseconds, thus providing a profile of dislocation behavior both during the stressing and immediately after the removal of the stress, i.e., during the very early stages of recovery. By adjusting the stress pulse "shape" it is also possible to obtain information on the behavior of dislocations while the stress is rising and falling. At the end of the initial fast sampling period, such sampling can be extended, or its rate can be decreased and the recovery process following the stress pulse application can be monitored over an extended period of time.

Principal Investigator: C. Elbaum (Physics and Applied Mathematics).

Personnel: A. Hikata (Applied Mathematics) and S. F. Hahn (Physics).

Effects of Strain Rate and Temperature on Plastic Deformation of Steels

A comprehensive experimental study involving static, dynamic and incremental strain rate plasticity experiments on low carbon cold-rolled and hot-rolled steels at temperatures ranging from -150°C to +110°C has now been extended for the hot-rolled steel to -190°C. An unexpected result of these latter experiments is an inverse strain rate history effect. This is seen in the fact that the flow stress in the dynamic portion of the incremental strain rate experiment is significantly greater than the flow stress resulting from loading entirely at the same constant dynamic strain rate. Furthermore, this inverse effect becomes more pronounced as the testing temperature is decreased. A possible explanation would involve thermal effects—the isothermal character of quasi-static straining in contrast to the nearly adiabatic conditions during dynamic straining. A technical report on this subject is being prepared. An oral presentation was made at the ASTM Symposium on Mechanical Testing for Deformation Model Development held in Bal Harbour, Florida in November 1980 and publication will be in an ASTM Special Technical Publication.

Dr. J. Klepaczko of the Institute of Fundamental Technological Research of the Polish Academy of Sciences in Warsaw has been a visitor at Brown since April 1, 1980. In the time he has been here he has initiated an extensive analysis of the results of experiments (some of which were conducted at Brown or at the Polish Academy of Sciences) with the goal of clarifying the source of strain rate sensitivity, strain rate history effects and temperature history effects in bcc metals—especially ferritic steels and iron. This study has resulted or will result in at least three technical reports:

1) "Recent Progress in the Understanding of Strain Rate and Temperature History Effects in bcc Metals," with J. Duffy, presented at the ASTM Symposium on Mechanical Testing for Deformation Model Development at Bal Harbour, Florida in November 1980. To be published in an ASTM Special Technical Publication.

2) "On Strain Rate and Strain Rate History Effects in bcc Metals and Ferritic Steels."

3) "Relation of Thermally Activated Flow in bcc Metals to Strain Rate and Temperature History Effects."

Experimental results including published results in the literature are being analyzed on the basis of thermally activated control of strain rate effects. A literature survey includes a search for evidence of strain rate history and temperature history effects in ferritic steels and other bcc metals.

Principal Investigator: J. Duffy (Engineering).

Personnel: J. Klepaczko (Engineering), R. H. Hawley (Engineering), G. J. LaBonte, Jr. (Engineering), P. Rush (Engineering), A. Rosakis (Engineering), and A. Morrone (Engineering).

Publications: "On the Uniqueness of Representation of the Stress Field of Plane Polygonal Dislocation Loops," A. J. Rosakis, Scripta Metallurgica *14* (1980), 1261-65.

"Strain Rate History Effects in LiF Single Crystals During Dynamic Loading in Shear," C. Y. Chiem and J. Duffy, Brown University Technical Report NSF ENG75-18532/11, July 1979. Accepted for publication in Material Science and Engineering.

Rate Theory

Methods previously developed for the study of quantum rate theory in a symmetric double-well potential have been extended to the asymmetric case. The approach involves the decomposition of the real stationary states into complex right- and left-moving states and the determination of exact transmission coefficients for the latter. Numerical solutions for a selection of representative parameter values were obtained for the time evolution of states which corresponded initially to a Gaussian wave packet localized in the upper well. Both resonant and nonresonant cases were studied and the significance of the transmission coefficient was established for each.

Principal Investigator: J. H. Weiner (Engineering).

Personnel: S. T. Tse (Engineering).

Publication: "Tunneling in Asymmetric Double-Well Potentials," J. H. Weiner and S. T. Tse, J. Chem. Phys., forthcoming (February 15, 1981).

Supported by the Materials Research Laboratory/NSF and the Gas Research Institute.

Crystal Elasticity

Theoretical calculations of the elastic moduli of crystals are generally based on assumed interatomic force laws which in turn are intended to reflect the electron states in the given system. In this work, the Hellmann-Feynman theorem has been used to derive a formula for the elastic moduli of centro-symmetric crystals directly in terms of the electron density and its distortion due to the crystal deformation. One consequence of this formula is the observation that these moduli satisfy the Cauchy relations if the electron density deforms according to the same affine transformation which governs the crystal deformation.

Principal Investigator: J. H. Weiner (Engineering).

Publication: "Hellmann-Feynman Theorem, Elastic Moduli, and the Cauchy Relations," J. H. Weiner, submitted to Phys. Rev.

Supported by the Materials Research Laboratory/NSF and the Gas Research Institute.

Plastic Shearing at Very High Strain Rates

Thin plate specimens ($\sim$0.4 mm thick) of aluminum sandwiched between two high strength steel plates have been subjected to shear strain rates of 10^4 - 10^5 s^{-1} by means of pressure-shear plate impact experiments. In these experiments, a flyer plate, inclined to the launch tube axis, impacts a parallel target plate assembly consisting of the specimen backed by a high strength steel plate. By using the pressure-shear configuration instead of the conventional normal impact configuration, it is possible to sustain high shear strain rates until unloading waves arrive from boundaries of the plates. Preliminary results indicate the feasibility of using such experiments to measure the flow stress at strain rates of 10^5 s^{-1}. For commercially pure aluminum these experiments show a marked increase in flow stress over the values reported for strain rates of 10^3 s^{-1}.

Principal Investigator: R. J. Clifton (Engineering).

Personnel: C. H. Li (Engineering).

Supported by the United States Army Research Office and the Materials Research Laboratory/NSF.

Shear Localization in Plastic Deformation

A previous quasi-static analysis of the stability of a pure shearing deformation has been extended to include the effects of inertia. As in the earlier quasi-static case, the analysis includes the effects of strain hardening, heat conduction, and the sensitivity of the flow stress to strain rate and temperature. Conditions are derived for the growth of infinitesimal variations from a homogeneous deformation. Explicit stability conditions are obtained for both the long and short wavelength limit as well as for the special case in which the material is modeled as a fluid with temperature dependent viscosity. Stability conditions for more general cases require determination of the roots of a polynomial of either degree 7 or degree 4, depending upon the level of generality retained.

Principal Investigator: R. J. Clifton (Engineering).

Supported by the United States Army Research Office and the Materials Research Laboratory/NSF.

Elastic-Plastic Wave Propagation

The situation of a step shear load which moves steadily on the surface of an elastic-plastic half space at a speed exceeding the elastic shear wave speed of the material has been examined. The orientation of the shear traction is such that the deformation is two-dimensional antiplane strain. Two different representations of the rate independent elastic-plastic material response have been considered. The first material model is based on the associated flow rule and the Mises yield condition with isotropic hardening, whereas the second model is based on a particular flow theory of plasticity which represents incremental behavior at a corner of the instantaneous yield surface. Both models predict the same response under the same proportional loading. The stress history experienced by a typical material particle during passage of the load step has been determined, and the variation of final strain with the magnitude of the load step has been calculated. One conclusion resulting from comparison of results for the two material models for this problem is that yield surface vertex formation is not significant in determining the final states of plastic strain.

Principal Investigator: L. B. Freund (Engineering).

Personnel: A. S. Douglas (Engineering).

Publication: "Shear Waves in an Elastic-Plastic Material Due to a Supersonic Surface Step Load," L. B. Freund and A. S. Douglas, Wave Motion 2 (1980), 159-165.

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

Pressure-Shear Waves

Symmetric impact of parallel plates inclined relative to the direction of approach have been used to study dynamic plastic deformation for loading along non-proportional stress paths. Further experiments on 6061-T6 aluminum appear to confirm that slip does not occur at the impact face for a 2:1 ratio of normal to transverse components of projectile velocity, provided that the impact surfaces are not highly polished. A series of experiments on α-titanium plates indicate that the wave profiles are similar in general appearance to those obtained for aluminum plates. However, more detailed comparisons suggest that strain rate sensitivity has a greater effect on the wave profiles for α-titanium. This conclusion follows from the observation that simple wave solutions cannot describe the observed wave profiles as well for α-titanium as for 6061-T6 aluminum.

- 6 -

Principal Investigator: R. J. Clifton (Engineering).

Personnel: A. Gilat (Engineering) and L. Hermann (Engineering).

Publication: "Pressure-Shear Impact of 6061-T6 Aluminum," K. S. Kim and R. J. Clifton, J. Appl. Mech. *47* (1980), 11-16.

SECTION 2

Fracture of Solids

Introduction

Studies on the fracture of solids encompass a wide range of problem areas in solid mechanics and materials science. One area given major emphasis has been microscale cavitation processes and the resulting prediction of macroscopic fracture ductility in terms of microstructure. Parts of this work are directed to elevated temperature diffusive creep rupture, with consideration of grain deformability and non-equilibrium cavity shapes (Needleman, Rice). Other work focuses on lower temperature cavitation processes, e.g., by a grain boundary splitting mode of ductile void growth in spheroidized steels (Gurland, Asaro), and on the effect of hydrogen on accelerating this process (Asaro). Further studies have used microscale models for ductile void growth as a basis for macroscopic, dilational plastic constitutive relations and, through finite element and other numerical analysis techniques, have led to assessments of effects of necking, triaxiality and strain rate on fracture ductility (Needleman, Saje).

A second area of major emphasis is that of plastic bifurcation and instability, particularly in the form of flow localization into a shear band as a precursor to ductile rupture. Some work in this area has continued the association established earlier between the constitutive description of double slip in fcc crystals and shear localization (Asaro, Needleman). Other works, directed to polycrystalline materials, employ recently developed models of vertex-like yielding as a basis for localization and bifurcation (Needleman). Studies appropriate to wrinkling bifurcations in sheet metal forming and surface bifurcations in non-homogeneously deformed bodies (e.g., beams in finite bending) have been done (Needleman, Abeyaratne). Also, a major accomplishment has been the development of finite element analysis procedures suitable for severely localized flow zones in the form of shear bands (Tvergaard, Needleman, Lo).

A further area of major emphasis is on the dynamic and non-linear analysis of crack growth. Crack toughness under high rate loading of steels has been measured and compared to static toughness (Duffy). Advances in computational techniques for dynamic crack propagation have been made, allowing also the possibility of elastic-plastic material response (Freund). A method based on caustics has been developed for incorporation of small scale plasticity effects in observational studies of dynamic crack tip fields (Freund, Duffy). The field of stress and deformation very near a stably growing tensile crack in an ideally plastic solid has been analyzed in further detail, and has served as basis for a predicted form of a ductile crack growth resistance curve shown to have experimental support for a high strength steel (Hermann, Rice). Further advances have been made on the analysis of crack tip fields in time-dependent materials, intended to model response under high temperature creep conditions (Kubo).

Also, major advances have been made on crack analysis under non-linear conditions in an idealized continuum model of fiber-reinforced composite materials (Pipkin).

A variety of other studies in solid mechanics and materials science have been carried out, involving, e.g., hydride formation and failure in zircalloy (Simpson), fracture mechanisms in two-phase alloys such as tungsten-carbide-cobalt (Gurland), oxidation failures in reaction-bonded nitride (Richman), cavitation in cobalt titanium alloys (Avery), crack tip fatigue processes in age-hardenable aluminum alloys (Asaro), shear fracture and crustal stress distribution processes in geomaterials (Lehner, Rice), constitutive descriptions of frictional slip (Rice), and other topics.

SECTION 2

Fracture of Solids

Individual Contributions

Analysis of Elastodynamic Crack Growth

Research has continued on the analysis of crack growth in nominally elastic materials at rates large enough for material inertia to be important. Work has been completed on the following projects:

a) The dynamic propagation of a crack in an anti-plane shear deformation field has been analyzed by second-order-accurate finite differences. The finite difference equations have been obtained by integrating the dynamic linear elastic equations of motion along the bicharacteristic strips in four perpendicular directions and the time axis to $O(\Delta t^3)$. The singularity in stresses around the crack has been calculated by performing a global energy balance on a small region containing the crack tip and approximating the stresses and velocity in this region by a one term asymptotic expansion about the crack tip. Results for stresses and stress intensity factor have been presented for a semi-infinite crack propagating steadily in an infinite strip, from which errors in the numerical calculations are identified. Cases of typical non-steady crack propagation in an infinite strip following steady propagation have also been considered.

b) The dynamic numerical analysis of linear elastic bodies containing a crack (stationary or propagating) has been carried out using four noded isoparametric finite elements with central differences in time. The crack tip region was represented by the one term asymptotic expansion of the near tip field where the stress intensity is obtained by performing an energy balance on a small region containing the crack tip. Examples of both Modes I and III crack propagation have been compared with analytic solutions.

c) The problem of an edge crack, propagating with constant velocity perpendicular to the traction free boundary of a linear elastic half space has been solved numerically for typical self-similar loading cases. A limiting case of uniform pressure on the crack faces has been shown to have a stress intensity factor close to that for the equivalent static problem, which serves as a check on the method. The effect of stress gradients has been demonstrated and, for impact loading, it is shown that cracks can only initiate under the center of the load if friction is present, and then only at very low crack tip speeds.

d) The plane strain response of an unbounded elastic body containing a semi-infinite crack subjected to a pair of concentrated forces suddenly applied to the crack faces at some distance from the crack tip has been determined. The forces act on opposite faces of the crack, in the plane of the crack, and in the *same* direction. An exact solution has been obtained within the framework of linear elastodynamics using a fundamental solution obtained from dynamic elastic dislocation theory. If the loading is quasi-statically applied, then the stress intensity factor is zero. However, if the loads are suddenly applied, the stress intensity factor varies with time and, for a short time, it takes on very large values. As time becomes large compared to the transit time of a Rayleigh wave from the load point to the crack tip, the stress intensity factor decays to zero.

Principal Investigator: L. B. Freund (Engineering).

Personnel: P. Burgers (Engineering) and I. S. Abou-Sayed (Engineering).

Publications: "Dynamic Linear Elastic Crack Propagation in Antiplane Shear by Finite Differences," P. Burgers, International Journal of Fracture *16* (1980), 261-74.

"Numerical Analysis of Dynamic Linear Elastic Fracture Mechanics Problems by Finite Elements," P. Burgers and L. B. Freund, Brown University Technical Report, February 1979.

"Dynamic Growth of an Edge Crack in a Half-Space," P. Burgers and L. B. Freund, International Journal of Solids and Structures *16* (1980), 265-74.

"The Stress Intensity Factor Due to Parallel Impact Loading of the Faces of a Crack," I. S. Abou-Sayed, P. Burgers, and L. B. Freund, Fracture Mechanics, ASTM STP 700, American Society for Testing and Materials (1980), 164-73.

Dynamic Elastic-Plastic Crack Growth

A numerical analysis of steady-state crack growth in an elastic-ideally plastic material under small scale yielding conditions has been performed. Crack growth is in the antiplane shear mode, and inertial resistance of the material to motion has been included explicitly. The numerical procedure is based on the finite-element method. It has been found that, with increasing crack tip speed, the active plastic zone becomes smaller and less concentrated in the direction of crack growth, and the crack tip plastic strain singularity becomes weaker. It has also been found that the rate of crack opening at a small distance behind the moving crack tip is insensitive to changes in crack tip speed.

A study was also completed on the analysis underlying the use of the optical method of caustics in fracture propagation experiments in metals. The shadow spot data which are obtained in using the method of caustics to determine experimentally dynamic stress intensity factors are usually interpreted on the basis of a static elastic crack model. In this work, an attempt was made to include both crack tip plasticity and inertial effects in the analysis underlying the use of the method of reflection. For dynamic crack propagation in the two-dimensional tensile mode which is accompanied by a Dugdale-Barenblatt line plastic zone, the predicted caustic curves and corresponding initial curves have been studied within the framework of plane stress and small scale yielding conditions. These curves have been found to have geometrical features which are quite different from those for purely elastic crack growth. Estimates have been made of the range of system parameters for which plasticity and inertia effects should be included in data analysis when using the method of caustics. For example, it is found that the error introduced through the neglect of plasticity effects in the analysis of data will be small as long as the size of the region near the crack tip which corresponds to the observed caustic is more than about twice the plastic zone size. Also, it is found that the error introduced through the neglect of inertial effects will be small as long as the crack speed is less than about 20% of the longitudinal wave speed.

Principal Investigator: L. B. Freund (Engineering).

Personnel: A. S. Douglas (Engineering), A. J. Rosakis (Engineering), and D. M. Parks (Engineering).

Publications: "Dynamic Steady Antiplane Shear Crack Growth in an Elastic-Plastic Material," A. S. Douglas, L. B. Freund, and D. M. Parks, Proceedings of the 5th International Conference on Fracture, Cannes, France, 1981.

"The Effect of Crack Tip Plasticity on the Determination of Dynamic Stress Intensity Factors by the Optical Method of Caustics," A. J. Rosakis and L. B. Freund, Brown University Technical Report N00014-0051/5, September 1980.

Fracture Initiation in Steel

In previous fracture initiation experiments with two low carbon steels (AISI 1018 cold-rolled and 1020 hot-rolled) the temperature ranges for cleavage fracture under quasi-static and dynamic loading conditions were established. In both instances microscopic examination of the specimens after testing showed that the fractures on the lower shelf initiate at carbide plates that precipitate along the ferrite grain boundaries, and that this result holds true for both quasi-static and dynamic loading. In order to pursue this subject further, and in collaboration with R. J. Asaro of our material science group, an investigation was undertaken to determine the fracture behavior of a similar steel with fewer and smaller carbide plates. AISI 1020 hot-rolled steel was modified by isothermal

transformation to significantly reduce in size and number the carbide plates along the grain boundaries. All other physical and mechanical characteristics were unaltered by this process and it was found that the plane strain fracture toughness, K_{IC}, is raised about 40% throughout the temperature region where cleavage fracture predominates, but is virtually unchanged at higher temperatures where ductile fractures prevail. A preliminary report is being prepared while further work is being accomplished which will track the source of cracks from the fracture surface to determine if the source is a carbide plate.

Principal Investigator: J. Duffy (Engineering).

Personnel: See below (Dynamic Crack Propagation).

Publications: See below (Dynamic Crack Propagation).

Dynamic Crack Propagation

A combined experimental and analytical study of crack propagation including development of a means for determination of the dynamic fracture toughness K_{Id} of a running crack in steel by the method of caustics is underway. The experiment will utilize a wedge loaded double cantilever beam specimen and a high speed 12-frame Crantz-Schardin type camera system. At the present time, we have photographed a number of single caustics produced by a running crack in 4340 steel; construction of the 12-frame camera has begun. A method of analyzing the caustics produced by a running crack has been developed.

Principal Investigator: J. Duffy (Engineering).

Personnel: R. H. Hawley (Engineering), G. J. LaBonte, Jr. (Engineering), P. Rush (Engineering), A. Rosakis (Engineering), and J. C. Lambropolis (Engineering).

Publications: "The Effect of Loading Rate and Temperature on Fracture Initiation in 1020 Hot-Rolled Steel," M. L. Wilson, R. H. Hawley, and J. Duffy, Engineering Fracture Mechanics *13* (1980), 371-85.

"Analysis of the Optical Method of Caustics for Dynamic Crack Propagation," A. J. Rosakis, Engineering Fracture Mechanics *13* ,1980), 331-47.

"The Effect of Loading Rate and Temperature on the Initiation of Fracture in a Mild, Rate-Sensitive Steel," L. S. Costin and J. Duffy, Trans. ASME, Journal of Engineering Materials and Technology *101* (1979), 258-64.

Supported by the Materials Research Laboratory/NSF, the National Science Foundation, the Office of Naval Research, and the Army Research Office.

Localization and Fracture of Solids

We have investigated numerically the possibility of localization in the Plane Strain Tensile Test using different constitutive relations. Localization was found to occur at reasonable strain levels, consistent with experimental observations. The effect of constitutive relation on the stress fields near the crack tip was also studied to see if classical plasticity theory with a smooth yield surface gives reasonable results under conditions of unloading and reloading. It was concluded that a constitutive relation which gives a different response for changes in loading directions does not affect the result significantly in the case that was studied.

Finally, a model which accounts for the residual plastic deformation at the flanks of a crack under cyclic loading is used to offer an explanation of crack growth retardation under changes in the level of loading.

Principal Investigator: K. K. Lo (Engineering).

Publications: "Flow Localization in the Plane Strain Tensile Test," K. K. Lo, V. Tvergaard, and A. Needleman, to appear in JMPS.

"Fatigue Crack Closure Under a Step Increase Load," K. K. Lo, to appear in J. Appl. Mech.

"Effect of Yield-Surface Vertex or Crack Tip Fields under Steady Mode III," K. K. Lo, to appear in JMPS.

Supported by the Materials Research Laboratory/NSF.

Failure of Fiber-Reinforced Materials

Plane deformations of fibrous and fiber-reinforced materials were studied by using mathematical models in which the fibers are treated as inextensible. Variants of the theory cover nets (1,2), closely-woven or coated fabrics (3), and stiff sheets with fibers in two orthogonal directions (4). Traction boundary-value problems lead to coupled non-linear integral equations that generally have more than one solution (5), some stable and others unstable. This general theoretical work provides the background for applications to tearing and crack problems (2). The theory is simple enough that although finite deformations are considered, it may be possible to predict dynamic crack or tear trajectories. Work on dynamic crack trajectories in small deformations is in progress.

Principal Investigator: A. C. Pipkin (Applied Mathematics).

Personnel: T. G. Rogers (Applied Mathematics) and L. Mannion (Applied Mathematics).

Publications: "Some Developments in the Theory of Inextensible Networks," A. C. Pipkin, Q. Appl. Math. *38* (1980), 343-55.

"Holes in Inextensible Networks," T. G. Rogers and A. C. Pipkin, QJMAM (forthcoming).

"Plane Traction Problems for Inextensible Networks," A. C. Pipkin, QJMAM (forthcoming).

"Finite Plane Stress of Stiff Fiber-Reinforced Sheets," A. C. Pipkin, JIMA (forthcoming).

"Boundary Integral Equations for Inextensible Materials," A. C. Pipkin, J. Elast. (forthcoming).

Supported by the Materials Research Laboratory/NSF, the National Science Foundation, and the Science Research Council (U.K.).

Fracture Initiation Criteria at Brittle, Second Phase Particles

The role of zirconium hydride as a fracture initiation site in Zirconium-2.5% Nb alloy has been studied. Experiments utilizing acoustic emission equipment were carried out to identify the precise conditions of stress and/or strain in the material, necessary to cause fracture of the hydride particles. Results showed that without development of triaxial stress conditions, fracture of the hydride particles was difficult, and they had little influence on fracture of the alloy (for the low hydrogen concentrations studied, $<$35 ug/g). On the other hand, hydrides cracked readily after some plastic deformations had occurred (ε_p<1%), if specimens were notched to produce a triaxial stress state. These results were explained in terms of a mechanism in which cracks were nucleated, in the hydrides, by slip bands impinging from the zirconium matrix. The stability of these cracks was dependent on the normal stress on the hydrides such that instability was favored by triaxiality.

Principal Investigator: L. A. Simpson (Engineering).

Publications: See below (Prediction of Ductile Fracture Conditions Using J-Resistance Curves).

Prediction of Ductile Fracture Conditions Using J-Resistance Curves

Raw data obtained prior to the author's arrival at MRL was analyzed to produce crack growth resistance curves for Zr-2.5% Nb, expressed in terms of the J-integral. These curves were used to predict the critical crack length in pressure tubes used in the CANDU nuclear reactor. A strong specimen dependence of R-curve shape was observed which was discussed in terms of current theories.

Initial experiments were also carried out on HY130 steel to determine J-resistance curves for conditions of small scale yielding through to full plasticity, to test the model of J. R. Rice. Project was incomplete at the end of the author's appointment, but is being continued by R. Asaro.

Principal Investigator: L. A. Simpson (Engineering).

Publications: "Expressions for Calculating J-Resistance Curves," L. A. Simpson, Int. J. Fracture *16* (1980), R247-R249.

"Effects of Specimen Geometry on Elastic Plastic R-Curves for Zr-2.5% Nb," L. A. Simpson, Fracture 1981, Proceedings of the 5th International Conference on Fracture, Cannes, France, April 1981, to be published by Pergamon Press.

"Criteria for Fracture Initiation at Hydrides in Zr-2.5% Nb Alloy," L. A. Simpson, submitted to Metallurgical Transactions, February 1981.

Supported by the Materials Research Laboratory/NSF and Atomic Energy of Canada Limited.

A Combined Macroscopic and Microscopic Approval to the Fracture of Metals

A systematic study of void nucleation at cementite particles in spheroidized steels during tensile deformation was completed. The favored sites for void nucleation were the interfaces of large particles situated on grain boundaries.

A criterion for void nucleation based on an analysis of the local stresses and elastic energy storage at spheroid particles in a plastically flowing matrix was developed. A critical normal stress requirement and energy balance consideration provided a double criterion for stable void nucleation.

Contributions to the stored elastic energy in the vicinity of the particles due to applied loading and local plastic incompatibilities were considered and models were evaluated for the present alloy systems in accordance with the proposed nucleation criterion.

Also completed was an experimental study of hydride cracking in zirconium alloys, using acoustic emission as a cracking indication.

Principal Investigator: J. Gurland (Engineering).

Personnel: L. A. Simpson (Engineering), J. R. Fisher (Engineering), and H. Stanton (Engineering).

Publications: "Void Nucleation in Spheroidized Steels During Tensile Deformation," J. R. Fisher, Ph.D. thesis, Brown University, June 1980.

"The Strength and Fracture of Two-Phase Alloys - A Comparison of Two Alloy Systems," J. Gurland, in *Fracture '79, Proceedings of the Conference on Fracture, University of the Witwatersrand, Johannesburg, South Africa,* 1979, p. 69.

"The Effect of Alloy Deformation on the Average Spacing Parameters of Non-Deforming Particles," J. R. Fisher and J. Gurland, Metallurgical Transactions, in press.

"Characterization of Hydride-Induced Slow Crack Growth in CANDU Nuclear Reactor Pressure Tubes,"

L. A. Simpson, MRL Technical Report, in preparation.

Strength and Fracture of Two-Phase Alloys

A study of the micro-mechanics of two-phase alloys has been initiated. The work was focused on the following aspects: 1) a quantitative discussion of spatial continuity of particulate aggregates, 2) consideration of the role of load transfer between soft and hard constituents, and 3) an experimental study of the yield and fracture of dual-phase steels.

An interesting preliminary conclusion is that load transfer is of considerable importance as a strengthening mechanism in this type of alloy. It is a function of the aspect ratio of the hard particles and of the connectivity of the hard constituent.

Principal Investigator: J. Gurland (Engineering).

Personnel: A. Szewczyk (Engineering) and H. Stanton (Engineering).

Publication: "An Approximate Method for the Estimate of the Contribution of Load Transfer to the Internal Stress in Dispersed Particles," J. Gurland, Scripta Metallurgica *13* (1979), 967.

Microstructure and Fracture Toughness of Cemented Carbides

Work continues on the theory of fracture of sintered WC-Co alloys. The initial strain energy release rate G_{IC} is related to the actually observed fracture process, namely intra- and transgranular fracture of WC, interfacial decohesion between carbide and binder, and plastic deformation to rupture of binder ligaments.

In addition, the crystallographic relations between contiguous WC grains in the sintered microstructure, have been studied experimentally and theoretically. The theory is based on the identification of coincidence lattice sites associated with low energy boundaries. The most frequent boundary configurations are being studied by measurement of dihedral contact angles and slip line directions in contiguous WC grains.

Principal Investigator: J. Gurland (Engineering).

Personnel: J. Hong (Engineering), R. Deshmukh (Engineering), and H. Stanton (Engineering).

Publication: "The Fracture Toughness of WC-Co Two-Phase Alloys - A Preliminary Model," M. Nakamura and J. Gurland, Metallurgical Transactions *11A* (1980), 141.

Shear Zones and Fracture

A common observation in certain highly deformed ductile solids is the more or less abrupt appearance of bands of highly localized deformation—shear bands—often leading to fracture along these zones. Analytical studies of certain aspects of this issue were conducted.

In the first paper (see below) the appearance of localized shear zones at the tip of a pre-existing crack in a nonlinearly elastic material was examined. An unsuccessful attempt was made to repeat this study in the case of a blunted notch. In the third paper, the initiation of shear bands at an imperfection site was examined considering

both hyper-elastic and hypo-elastic constitutive relations.

The second paper is unrelated to these studies. It presents the solution of a rather elementary boundary-value problem in the theory of large strain plasticity.

Principal Investigator: R. C. Abeyaratne (Materials Research Laboratory).

Publications: "Discontinuous Deformation Gradients Away from the Tip of a Crack in Anti-Plane Shear," R. Abeyaratne, to appear in Journal of Elasticity.

"Finite Elastic-Plastic Deformation of a Rotating Hollow Cylinder," K. K. Lo and R. Abeyaratne, submitted for publication to the Journal of Applied Mechanics.

"On the Emergence of Shear Bands in Plane Strain," R. Abeyaratne and N. Triantafyllidis, to appear in International Journal for Solids and Structures.

Supported by the Materials Research Laboratory/NSF.

Single Crystal Constitutive Laws

Pierce, Asaro, and Needleman are continuing work on large strain single crystal deformation. Assuming physically plausible forms for the slip-system hardening moduli, we are using Asaro's constitutive formulation to calculate important macroscopic features in a tensile test. For the three-dimensional crystal, the effects of latent hardening on lattice rotations and overshoot of the ‹100›-‹111› symmetry boundary have been quantitatively analyzed (D. Pierce, M.Sc. thesis). In addition, critical conditions for the onset of shear localization, viewed as a bifurcation from a homogeneous deformation state, have been determined. A significant result, as in Asaro's two-dimensional analysis, is the admissibility of bifurcation while the slip systems are still strain-hardening. To further our study, we are again concentrating on the two-dimensional model, but, by means of the finite element method, we hope to understand better the effects of inhomogeneous deformation (especially necking) on the inception of a localized mode. This more complete understanding of single crystal behavior will allow us next to develop an appropriate description of polycrystalline deformation at finite strains.

Principal Investigators: R. J. Asaro (Engineering) and A. Needleman (Engineering).

Personnel: D. Pierce (Engineering).

Publication: "Latent Hardening and Overshoot in the Deformation of Single Crystals," D. Pierce, M.Sc. thesis, Brown University, June 1980.

Supported by the Materials Research Laboratory/NSF.

Flow Localization in Porous Solids

Ductile metals, when highly deformed, are prone to the localization of deformation in the form of shear bands. Often such metals contain second phase particles which may crack or debond from the surrounding matrix material and the voids thus nucleated then grow by plastic deformation. A rate independent constitutive model of a porous plastic solid developed by Gurson has been employed to investigate the influence of void nucleation occurring during the deformation history on shear localization. Both plastic strain-controlled and stress-controlled nucleation processes are simulated. Two deformation histories are considered, one corresponding to uniaxial tension and the other to plane strain tension. The enhanced triaxiality at the center of a neck is simulated by application of Bridgman's solution for the stress and deformation state at the minimum section of a necked bar.

For the rate independent version of the study, the enhanced triaxiality due to necking is found to have great influences on flow localization in uniaxial tension, the necking has reduced the localization strain by about a factor of two, but the necking only has moderate effects on flow localization in plane strain tension. The destabilizing

effect that arises when void nucleation is stress-controlled and nucleation occurs over a narrow range of stress is illustrated. Results are obtained by employing parameter values representative of spheroidized carbon steels employed in a recent experimental study carried out by Fisher (Ph.D. thesis, Brown University, 1980), and the predictions of the model are in good agreement with experimental observations.

In a companion study, the effect of plastic strain-rate sensitivity on localization has been analyzed. The parameter values, representative of the above-mentioned steels studied by Fisher and the rate sensitivity of 1018 cold-rolled steel reported by the experimental results of Costin *et al.* are employed to characterize a porous solid, and the numerical predictions of the localization strain in axisymmetric tension with necking are in good agreement with the fracture strains obtained experimentally and, therefore, with those given by the rate independent analysis. However, the present numerical predictions of localization show that the material rate sensitivity raises the localization strain in plane strain tension more than in axisymmetric tension. The ductility ratio, the ratio of the localization strain in plane strain tension to that in axisymmetric tension, is found to increase significantly from the value of the corresponding rate independent analysis.

Principal Investigators: A. Needleman (Engineering) and J. R. Rice (Engineering).

Personnel: J. Pan (Engineering) and M. Saje (Engineering).

Publication: "Void Nucleation Effects on Shear Localization in Porous Plastic Solids," M. Saje, J. Pan, and A. Needleman, submitted for publication.

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

Plastic Shear Localization from Inhomogeneous Deformation States

Localization of plastic flow in narrow shear bands is frequently observed in ductile metals subject to tensile or compressive loading. The growth of such shear bands has been previously analyzed in cases where the stress state outside the band is homogeneous and the band is assumed to have constant width. In an ongoing series of studies the initiation and propagation of localized shear deformations in solids subject to non-uniform states of deformation is being analyzed.

In the plane strain tensile test, the deformations are observed to remain essentially homogeneous up to the maximum load point after which a diffuse neck develops. Then, for structural metals the deformation mode often shifts to one involving a band or bands of high localized shear. Previous numerical studies have employed the simplest *smooth yield surface theory of plasticity and have found continued growth of the diffuse neck, with no tendency* exhibited for the deformation pattern to shift to one involving intense localized shearing. It was not surprising that these numerical studies gave no indication of shear band formation since studies of material instability reveal that the classical smooth yield surface elastic-plastic solid is quite resistant to localization of deformation into a shear band (Rice, p. 207 in Proc. 14th IUTAM Congress, Delft, 1976). One feature of the plastic response of polycrystals is that the incremental tensorial relations between strain and stress are expected, within a rate-independent model, to exhibit a "vertex" structure. This means that the direction (in an appropriate hyperspace) of the strain increment is at least somewhat dependent on the direction of the stress increment, in contrast to classical constitutive models of the Prandtl-Reuss-Mises type. This feature leads to localization instabilities at sufficiently reduced strain hardening levels.

A finite element analysis of the plane strain tensile test for a solid that develops a vertex on its yield surface has been carried out. The phenomenological J_2 corner theory of Christoffersen and Hutchinson (J. Mech. Phys. Solids 27, (1979), 465) was employed. In this J_2 corner theory the instantaneous moduli are associated with those of a finite strain generalization of J_2 deformation theory for nearly proportional loading. For increasing deviation from proportional loading the moduli stiffen smoothly until they coincide with the linear elastic moduli for stress rates directed along or within the corner of the yield surface. A variety of initial thickness imperfections were also considered. One component of the imperfection was always taken in the form of the diffuse necking mode. Additional shorter wavelength imperfections were included in some of the computations.

In all cases the numerical calculations exhibited a transition from the diffuse necking deformation pattern to one *having well defined shear bands. The particular shear band pattern that emerged depended on the initial*

imperfection. Among the notable features of the numerical results were: (i) that the shear bands tended to propagate along the orientation revealed by a "material instability" analysis to be most critical for bifurcation into the shear band mode and (ii) that secondary shear band patterns emerged after a well developed primary shear band pattern had formed.

We continued our study of the development of flow localization from nonhomogeneous deformation states by considering shear band development in a plate subject to pure bending. One motivation for focusing on this problem stems from applications to various metal forming processes which involve bending of sheet metal. Bending beyond a certain minimum radius of curvature relative to the plate thickness can lead to shear fracture at the surface. The possibility of bifurcation away from the cylindrically symmetric fundamental state of pure bending has been studied by Triantafyllidis for an incompressible nonlinear elastic solid. The critical bifurcation mode is a surface wave mode, which occurs first in the compressive region, with the shortest possible wavelength being critical. Subsequently, if the fundamental, unbifurcated state is thought to be continued beyond the first critical bifurcation point, ellipticity of the governing equations is lost at the surfaces. Thus, the bifurcation behavior in pure bending, where a short wavelength mode is most critical, contrasts with that in plane strain tension, where the mode with the longest possible wavelength is most critical. Triantafyllidis' bifurcation results do not hold directly for an elastic-plastic solid since in pure bending strongly nonproportional loading takes place prior to bifurcation. However, near the surface regions that are most highly stressed and thus most important for bifurcation proportional loading does occur.

We carried out a numerical study of shear band development in a plane strain strip subject to pure bending employing the same two material models as used in our plane strain tension study. In some of the calculations the material parameters employed in this study were identical to those used in the plane strain tension analysis.

The shear band patterns that developed for the J_2 corner theory solid, with strain hardening, resembled those associated with the formation of a plastic hinge in an ideally plastic solid. The location and number of these "hinges" depended on the specified initial thickness inhomogeneity but the pattern of shear bands forming the hinge was similar in each case considered.

In pure bending, the shear bands must propagate inward against an adverse deformation gradient so that the peak straining occurred at the free surface. In contrast, in plane strain tension, due to diffuse necking, the most intense shearing can occur in the interior of the specimen. In the pure bending case we found that intense surface oscillations occurred where the shear bands met the free surface on the compressive side of the plate. Our results indicate that in pure bending of a plate made of a material prone to shear band development, the protuberances that develop from these oscillations would serve as likely failure initiation sites.

Principal Investigator: A. Needleman (Engineering).

Personnel: N. Triantafyllidis (Engineering), K. K. Lo (Engineering), and V. Tvergaard (Engineering).

Publications: "Bifurcation Phenomena in Pure Bending," N. Triantafyllidis, J. Mech. Phys. Solids 28, (1980), 221.

"Flow Localization in the Plane Strain Tensile Test," V. Tvergaard, A. Needleman, and K. K. Lo, J. Mech. Phys. Solids, in press.

"On the Development of Shear Bands in Pure Bending," N. Triantafyllidis, A. Needleman, and V. Tvergaard, submitted for publication.

Wrinkling in the Swift Cup Test

We analyzed the onset of wrinkling in the Swift cup test, which is used to determine the drawability of sheet metals. In this test a flat sheet, held at its periphery between a dieblock and a blankholder, is drawn into a cup by a cylindrical punch. The term wrinkling refers to a failure mode involving the formation of buckles (or wrinkles) in the flange, which is the portion of the sheet remaining between the die and the blankholder. We modelled the flange as an annular plate subject to axisymmetric radial tension along its inner edge. A numerical solution to the

bifurcation problem governing the onset of wrinkling was obtained by employing separation of variables in conjunction with a finite element method. The sheet material was characterized both by the simplest flow theory of plasticity and by the simplest deformation theory of plasticity. In each case isotropy was presumed to hold in the plane of the sheet but normal plastic anisotropy was accounted for. The restraint provided by the blankholder was modelled by resting the annular plate on a linear elastic foundation.

We found that the critical drawing displacement for the onset of wrinkling, with a blankholder present, increased with increasing plastic anisotropy. These results which were obtained employing deformation theory were consistent with experimental observations of Naziri and Pearce (La Metall. Italiana, No. 8 (1968), 727) who found that the blankholder load required to suppress wrinkling decreased with increasing plastic anisotropy. Our results also indicated that if an attempt were made to investigate the effect of plastic anisotropy on wrinkling without a blankholder, the effect would not be observed. Previous analyses which were carried out within a framework of beam theory or which restricted attention to the simplest flow theory of plasticity did not reveal the dependence of the onset of wrinkling on the plastic anisotropy.

Principal Investigator: A. Needleman (Engineering).

Personnel: N. Triantafyllidis (Engineering).

Effects of Hydrogen on Fracture

Cialone and Asaro have recently completed an experimental study of the effects of hydrogen on ductile fracture in plain carbon steels. Results on two steels, viz. a 1017 and a 0.15 wt percent carbon steel have shown that hydrogen affects both the process of void initiation at cementite particles and void growth leading to a significant loss in ductility. The results are consistent with the view that hydrogen reduces the cohesive strength of the particle-matrix interface thereby facilitating decohesion. Void growth, which appears to occur to a large extent along grain boundaries, is also accelerated by hydrogen and, again, the results suggest that hydrogen has the effect of reducing the cohesion of the interface, in this case grain boundaries. These results are consistent with our earlier results on a 1045 plain carbon steel. In these lower carbon steels, however, we observed a transition in the fracture mode with increasing hydrogen content from ductile void initiation and growth to transgranular cleavage. The tendency for cleavage was found to be dependent upon microstructure. In fact, a good correlation was found between the total amount of interface (grain boundary, particle-matrix, etc.) and the susceptibility to cleavage; less interface was associated with an increased occurrence of cleavage.

Principal Investigator: R. J. Asaro (Engineering).

Personnel: H. Cialone (Engineering).

Oxidation and Fracture Characteristics of Reaction Bonded Silicon Nitride (RBSN)

The application of high strength ceramic materials for high temperature turbine engines and components not only requires that these normally brittle materials have strength, toughness, and creep resistance at elevated temperatures, but also that these materials stand up to the hot corrosive and erosive atmospheres within the turbine engines and that any oxidation suffered by the ceramic materials does not result in a degradation of these properties. Oxidation studies of RBSN have been conducted to determine microstructurally the path of oxidation in the various phases and microconstituents present in the material when used in turbine engine applications. The oxidation of unreacted silicon, the oxidation of silicon nitride, and the penetration of grain boundaries and surface flaws by these brittle oxides leads to the creation of Griffith flaws which were not present when the part was fabricated. The continued utilization of ceramic turbine engine components of RBSN is dependent on understanding the effect of microstructural oxidation and crack formation and growth and also upon the development of techniques and processes for rendering the surfaces of these materials oxidation resistant or retardant. Such treatments are being investigated at the present time with the view that a new generation of RBSN will be fabricated which will be resistant to oxidation and hot corrosion and which will allow greater turbine engine life.

Principal Investigator: M. H. Richman (Engineering).

Personnel: M. Magida (Engineering), O. Gregory (Engineering), and J. Fogarty (Engineering).

Publication: "Effect of Processing Parameters on Reaction Bonding of Silicon Nitride," M. H. Richman, to appear as NASA-Lewis Technical Report.

Supported by the Materials Research Laboratory/NSF and the National Aeronautics and Space Administration (Lewis).

Shear Rupture of Geological Materials

Work on brittle-elastic stress-strain behavior of compressed rock by Kachanov was based on a model in which frictional sliding on microcracks, accompanied by the growth of secondary (tensile) cracks, is the dominant mechanism of inelasticity. An approximate theoretical description of branched frictional sliding cracks, which took into account uplifting at asperities, was constructed. It was found that most of the features of pre-peak macroscopic behavior, before extensive crack interaction, could be reasonably well described by the model. The fracture toughness K_{IC} inferred from the model, based on observations of the onset of dilatant deformation in various rock tests, is relatively constant and has values in the range of those determined directly from macro-scale crack propagation fracture tests. Time-dependent crack growth (stress corrosion cracking) was also considered in the framework of the model, as a source for creep of compressed rock in the elastic-brittle range.

Experimental studies of sliding friction on smooth rock surfaces by Ruina, in collaboration with Dieterich at the latter's laboratory at U.S.G.S., Menlo Park, provided a number of significant results. It was observed that for steady slip (at fixed normal stress) of sandwich-type quartzite specimens the friction coefficient μ approached (with ongoing slip) a decreasing function of sliding velocity, V^*, which was independent of previous slip history. However, if the slip velocity was suddenly changed from V^* (at which steady state has been achieved) to another value V, the *sudden* change $\Delta\mu$ in the friction coefficient was positive for $V \cdot V^*$ and negative for $V \cdot V^*$. That is, the sudden change in frictional resistance occurs in a sense opposite to the long-term change. On a plot of μ versus slip distance, the result for a transition from speed V_1 to V_2 is very nearly the mirror image of that for a transition from V_2 to V_1.

The total friction coefficient μ can be written as $\mu = \mu_\ell + \mu_s$, where μ_ℓ and μ_s are long-term and short-term components respectively. The long-term component μ_ℓ of frictional resistance was found to approach the steady state resistance, given by, say, $\mu = g(V)$, at a rate that depends on the difference between μ_ℓ and $g(V)$. This result can be fit well by:

$$d\mu_\ell/dt = -(V/d_\ell)[\mu_\ell - g(V)],$$

where d_ℓ is a characteristic slip distance ($d_\ell \sim 5.2\mu m$ for the quartzite surface examined). Short-term decay which is responsible for the sudden increase in friction associated with $\Delta\mu$ is also fit tolerably by an exponential

decay of the form:

$$d[\mu_s\text{-}f(V)]/dt = -(V/d_s)\mu_s$$

where the characteristic slip distance $d_s \approx 0.32\mu m$ is much smaller than d_r, and $f(V)$ represents a direct velocity dependence associated with the sudden increases in friction with rapid velocity increases mentioned above. The two differential equations for μ_r and μ_s, together with the steady state resistance function $g(V)$ and the direct velocity dependence function $f(V)$ seem to provide an adequate constitutive model for the results so far observed. Over the range of velocities tested (approximately 0.01 to 1 $\mu m/sec$) these two functions are well described as linear functions of log V.

Work has also been completed on the mechanics of elastic lithosphere/viscoelastic asthenosphere coupling in time-dependent stress redistribution along rupturing plate boundaries. A generalized Elsasser-type plate foundation model allowing for a Maxwellian viscoelastic asthenosphere, formulated earlier by Rice, has been analyzed by Lehner, Li, and Rice for spatial and temporal stress alterations associated with suddenly introduced or migrating (crack-like or dislocation-like) ruptures along finite segments of transform or subduction-type plate boundaries. The stress which is shed by a great earthquake onto the asthenosphere is gradually transferred back to the lithosphere by a relaxation process. Accordingly, it was found that the post-seismic increases in stress outside the rupture zone might exceed the coseismic elastostatic stress alterations several times and amount in magnitude to an appreciable fraction of the stress drop on the fault. For example, in the distributed dislocation model with fixed slip distributions due to a uniform stress drop of 100 bars on the ruptured fault, the stress alteration at one lithospheric distance ahead gradually increases to about 18 bars at a rate comparable, for several years after the rupture, to that due to plate motion corresponding to repeat times of 100 years. Such stress transfer may contribute significantly to the triggering of large earthquakes in adjacent segments of the plate boundary. When post-seismic slippage along the fault is unimportant, the stress on the fault will build up in time due to the same mechanism of asthenosphere relaxation. The spatial and temporal characteristics of this post-seismic stressing were found to be quite distinct for points located on the rupture and beyond it, suggesting characteristic patterns of prolonged aftershock activity for locations inside and outside a new rupture zone.

Migration of seismic activity along a plate boundary has been modelled by a steadily advancing zone of stress drop. The altered stress state propagating ahead of this zone is found to correspond very closely to an essentially unrelaxed state of the asthenosphere at typical propagation speeds of 100 km/yr. When arrested by a barrier, a disturbance of this kind can transfer significant stresses to the barrier from a then relaxing asthenosphere as described above, and could thus act as a delayed trigger to a barrier breaking event.

Principal Investigator: J. R. Rice (Engineering).

Personnel: F. K. Lehner (Engineering), R. Dmowska (Geological Sciences), V. C. Li (Engineering), A. Ruina (Engineering), and M. Kachanov (Engineering).

Publications: "The Mechanics of Earthquake Rupture," J. R. Rice, in Physics of the Earth's Interior (Proc. Int. School of Physics "Enrico Fermi," Course 78), ed. A. M. Dziewonski and E. Boschi, Italian Physical Soc./North Holland (1980), pp. 555-649.

Contribution to discussion on "Outstanding Problems of Geodynamics: Mechanisms of Faulting," J. R. Rice, ibid., pp. 713-16.

"Microcrack Model for Rock Inelasticity," M. L. Kachanov, Ph.D. thesis, Brown University, 1980.

Supported by the National Science Foundation (Geophysics Program) and the U.S. Geological Service.

Elastic-Plastic Analysis of Ductile Crack Growth

Work on crack growth in ductile metals has been based on a combination of analytical work on the structure of elastic-plastic strain field singularities, numerical finite element studies, and experimentation on plane-strain mode growth in steels.

An experimental investigation carried out by Hermann and Rice assessed the accuracy of a stable crack growth criterion proposed on the basis of earlier theoretical work by Rice, Drugan, and Sham. These theoretical results combined an approximate asymptotic analysis with numerical finite element studies to determine the stress and deformation fields very near the tip of a growing crack in an elastic-ideally plastic material. Knowledge of these near-tip fields allowed statement of explicit conditions for variation of J with crack length, at small scale yielding, to meet a fracture criterion which hypothesized a self-similar deformation state near the crack tip during growth. The experiments were an extension of work by Odegaard and Asaro on high strength 4140 steel, now heat treated to a relatively brittle condition to facilitate significant stable crack growth before conditions of general yielding were met. This was done because the theory is fully developed only for crack growth with well-contained yielding. The work consisted of testing four pre-fatigued compact tension specimens, continuously recording the load P and the opening displacement Δ along the load line, for crack growth from the small scale yielding range up through the general yielding configuration (representing a substantial amount of stable crack growth, e.g., 4 to 9 mm before general yield). A differential compliance technique was used to measure amounts of stable crack growth; total compliance-estimated growth differed from visually observed growth at the end of each test by less than 7% in the worst case.

Curves showing the experimentally-determined dependence of the "deformation theory" value of the J-integral, J_d, on crack length a were plotted for each specimen and compared with the theoretical curves of J_d versus a obtained by integrating the expression for dJ da given by the small-scale yielding theory of Rice, Drugan, and Sham:

$$dJ da = (\beta \cdot \alpha)(\sigma_0^2 E) \ln (\rho/eR).$$

Here E is Young's modulus, σ_0 is the tensile yield strength, J is the far-field value of the J-integral, a is the crack length, e is the natural logarithm base. $\beta \approx 5.1$ for $\nu = 0.3$; correlation with the finite element results for small scale yielding suggested $\alpha = 0.65$ and $R \approx 0.23 \ EJ/\sigma_0^2$. The parameter ρ governs the intensity of near-tip crack opening. and is a material-dependent constant for the hypothesized criterion of growth with a constant near tip profile. The constant was chosen to provide the best fit of the theoretical curves with the experimental ones. Proceeding in this manner, good theoretical to experimental correlation was found over the entire range of stable crack growth prior to general yielding.

A recently completed analytical investigation by Rice develops a procedure for exact elastic-ideally plastic asymptotic analysis of fields at tips of growing cracks under various conditions. Previous plane strain solutions have been based on the approximation that the yield condition reduces to a planar form of constant resolved shear stress in all plastically active sectors near the crack tip, arguing that since this is known to be true in plastic sectors of singular strain, it is approximately correct for all plastic sectors. The new formulation treats the yield condition as fully three-dimensional in non-singular plastic sectors, showing that for an exact solution the stress fields in such plastic sectors are not statically determinate. A compatibility condition is required, and formulated, to determine the full set of equations which govern the asymptotic field. This study also extends the concepts developed previously, for asymptotic analysis of crack problems in specific limited cases, to crack growth with arbitrary combinations of tensile and shear loading modes in materials with arbitrary anisotropy of elastic moduli and (ideally) plastic yield condition. Among the results of the study, centered fan sectors of singular straining at the crack tip are shown to be a general feature of the large class of material response treated, as are also the plastic strain singularity types associated with stationary and growing cracks.

A final finite element solution for a stably growing crack under small-scale yielding and plane strain conditions in an elastic-ideally plastic solid was initiated by T-L. Sham in an effort to improve the accuracy with which the undetermined parameters arising in the asymptotic crack tip analysis are known. The procedure is based on the minimization of a modified energy functional, written in the spirit of Hilton and Hutchinson (Engrg. Frac. Mech., 1971) for incremental plasticity under small displacement gradient assumptions. In this procedure, the field quantities in the elastic region away from the crack tip are represented by series convergent at large distances from the tip in terms of unknown coefficients. The leading term in the series is characterized by a specified stress intensity K; this term is the one for which stresses decay as $r^{-1/2}$. The near-tip region, where the material response is elastic-plastic, is discretized into finite elements in the usual manner. The nodal displacement increments along the boundary of these two regions are taken to be those given by the series representation, and the discrete, incremental equilibrium equations are obtained through the minimization of the modified energy functional. The advantage of this procedure is that the small scale yielding conditions are always met irrespective of the size of the plastic zone inside the finite element mesh, and we can concentrate all the available finite element degrees of freedom (which are limited by the computer capability) in the plastic zone and region nearby.

A parallel finite element investigation was begun by Sham, Tse, and Pan on the generation of a stable crack growth solution which progresses from small scale yielding to general yield conditions for the deeply cracked bend specimen geometry. This geometry and loading mode correspond closely to our experimental specimens, and the work has the dual purposes of showing how the parameters which are undetermined by the asymptotic analyses vary through the range from small scale yielding to general yield, and also, therefore, of permitting comparison between the theoretical growth equation and actual experimental results all the way up to and through the general yielding range.

Work on creep crack analysis was also in progress. Kubo investigated the nature of near-tip fields of stationary cracks in solids characterized by the Bailey-Orowan viscoplastic model:

$$\dot{\epsilon}_{ij} = FS^{n-1}(\sigma'_{ij} - \alpha_{ij})$$

$$\dot{\alpha}_{ij} = (C\dot{\epsilon}_{ij}/\alpha^\beta) - D\alpha^{n-\beta-1}\alpha_{ij}$$

where α_{ij} is the "internal stress" parameter, n, β, C, D, and F are material constants, and α and S are defined as

$$\alpha = \sqrt{\alpha_{ij}\alpha_{ij}}$$

$$S = \sqrt{(\sigma'_{ij} - \alpha_{ij})(\sigma'_{ij} - \alpha_{ij})} .$$

This model can account for creep recovery, thought to be one of the causes of high crack growth rates under cyclic or variable loadings at high temperatures. One important result of the work thus far is the determination that HRR singular fields prevail in the vicinity of the crack tip for any combination of material parameters. Kubo is analyzing the time dependence of their amplitude, in response to step loading.

Principal Investigator: J. R. Rice (Engineering).

Personnel: W. J. Drugan (Engineering), L. Hermann (Engineering), T-L. Sham (Engineering), H. Pan (Engineering), and S. Kubo (Engineering).

Publications: "Comparison of Theory and Experiment for Elastic-Plastic Plane Strain Crack Growth," L. Hermann and J. R. Rice, Metal Science *14* (1980), 285-91.

"Elastic-Plastic Crack Growth," J. R. Rice, in Mechanics of Solids: The Rodney Hill 60th Anniversary Volume, ed. H. G. Hopkins and M. J. Sewell, Pergamon Press, Oxford, in press.

Supported by the Materials Research Laboratory/NSF and the U.S. Department of Energy.

Elevated-Temperature Creep Cavitation of Grain Boundaries

Under creep conditions, polycrystalline solids often rupture prematurely due to the diffusive growth and coalescence of grain boundary voids. Driven by stress gradients, matter diffused from the void surfaces is deposited along the grain boundaries. Previous analyses of the problem have mainly been based on the assumption that the grains adjoining the cavitating boundary separate rigidly. Our recent studies have investigated the effect of grain deformability. Needleman and Rice have analyzed the growth of cavities along grain interfaces by the combined processes of grain boundary diffusion and plastic dislocation creep in the adjoining grains. The formulation of the problem and the finite element scheme employed are based on a variational principle, which governs the combined processes described above.

The principal effect is that creep deformability of the grains allows matter diffused from the cavity walls to be accommodated by local separations of the adjoining grains in the vicinity of the cavity, thus shortening the effective diffusion path length and allowing high values of the local matter flux. In turn, this results in greater rates of cavity growth than would be the case if either grain boundary diffusion or plastic creep flow acted alone.

The interaction between plastic creep and diffusion is shown to be characterized by a parameter L, which has

dimension of length and which is a function of material properties (which arise in describing g.b. diffusion and dislocation creep), temperature and applied stress. L decreases with increasing temperature and stress and (for various pure metals stressed to 10^{-3} x shear modulus at 0.5 T_M) L has values in the range 0.25 to 25 μm. The contribution of dislocation creep to the cavity growth rate is shown to be negligible when L is comparable to or larger than the cavity spacing, but significant interactions occur, leading to growth rates very much in excess of those predicted on the basis of boundary diffusion alone, when L is comparable to or smaller than the cavity size.

Needleman and Sham have begun an examination of the effect of stress triaxiality on cavity growth for the same axisymmetric cavity growth mode: work thus far discussed was for uniaxial tension. Limited results thus far for nonlinear viscous materials suggest that due to triaxiality, the range where the interaction between creep and diffusion is important changes in comparison with the zero hydrostatic stress case. The analysis in this area is continuing.

The work cited thus far has assumed that surface diffusion is rapid enough that a quasi-equilibrium spherical-cap cavity shape is retained. However, the analysis of the interaction between plastic creep and diffusion predicts a growth rate so rapid, at high stress levels, that this condition will not always be met. Consequently, Rice and Sham are studying the effect of non-equilibrium cavity shapes on cavity growth for the combined processes of creep and diffusion. Work has been directed toward determining the cavity profile in the limiting case of rapid growth in the crack-like mode with deformable adjoining grains. A preliminary study has been made on the cavity profile in the crack-like mode, when the adjoining grains are moving apart rigidly with a velocity of $\dot{\delta}/2$. Here δ is the effective thickening at the grain boundary. It is found that the cavity profile is affected only through the combination $\dot{\delta}\cdot 2v$ where v is the cavity growth speed. The conditions under which this contribution is important are being examined.

In order to understand elastic relaxation effects, at low stress conditions for which there is negligible plastic flow, a coupled elasticity-diffusion problem has been formulated by Rice and Rubinstein. The response of partially damaged materials (where damage is represented as crack-like cavities on grain boundaries) following load alterations is analyzed. Again, there is material redistribution from the void surfaces to the grain boundaries, and in this case non-uniform matter accommodation along boundaries is accomplished by elastic deformation.

These coupled phenomena are modelled in terms of a boundary value problem for the elastic stress field, which is constrained to satisfy the grain boundary diffusion and transport conservation equations on the grain boundary, and to obey stress free conditions at the crack-like cavity surfaces. On the basis of the solution for the stress field produced by a dislocation suddenly introduced on the grain boundary, integral equations have been derived for both single crack and periodically distributed cracks on the grain boundary. The integral equations have been solved numerically by Rubinstein for the case of cyclic loading, and Fourier superposed solutions have been developed for sudden step loadings.

For the suddenly applied loading, the results demonstrate that the elastic stress concentration is effectively relaxed by diffusion after time t = 0.05τ, where $\tau \approx \ell^3/DE$, ℓ is half of the distance between adjacent tips of neighboring cracks along the grain boundary, E is Young's modulus, and D is the diffusion parameter relating volumetric flux along the g.b. to stress gradient. By t = 0.25τ the stress distribution becomes essentially identical to that for rigid grains, i.e., diffusion has become the dominant process.

Principal Investigators: A. Needleman (Engineering) and J. R. Rice (Engineering).

Personnel: A. Rubinstein (Engineering) and T-L. Sham (Engineering).

Fatigue of Aluminum Alloys

This research is concerned with a study of the macro- and micro-mechanics of fatigue crack growth in an age-hardenable aluminum alloy, e.g., 2048 aluminum. Special attention is given to the importance of microstructure, including grain size and aging treatment in crack growth, on the phenomena of crack tip closure, and on overload retardation effects. Crack closure is being studied in detail throughout the course of this research program and its use in describing crack growth explored.

This research has led to the further refinement of experimental techniques used to measure in-situ crack growth. This, in turn, has led to the development of some new apparatus for measuring small changes in specimen compliance and thus small increments of crack growth.

The present program has also allowed us to build a computer interface with our closed loop testing equipment. This is now working as a data acquisition system.

Principal Investigator: R. J. Asaro (Engineering).

Personnel: L. Hermann (Engineering) and J. M. Baik (Engineering).

Publications: "Transitions in Fatigue Crack Closure in 2048 Aluminum," R. J. Asaro, L. Hermann, and J. M. Baik, to appear in Met. Trans.

"Fatigue Crack Growth in 2048 Aluminum," J. M. Baik, L. Hermann, and R. J. Asaro, in preparation.

Strength and Fracture in High Strength Titanium Alloys

Attention during the past year focused on thermomechanical processing of Cobalt Titanium Alloys. Alloys of CO-5, 6, 7, 10 and 18% Ti were prepared.

These consist of a two phase mixture of HCP CO with a very low stacking fault energy and γ, CO_3Ti, which is an ordering fcc alloy of the Cu_3Au type. After annealing at 1100°C and quenching, the alloys were ductile and could be cold rolled in excess of 50%. Strength determined by hardness increased rapidly and tended to a maximum for the 10% Ti alloy equal volume fractions of both phases. Hardness reached Rc 36 at 8% cold deformation and Rc 40·42 at 50%. With low temperature aging treatments hardness increased to Tc 48 to 50. From previous experience with β titanium alloys we expect the aging treatment to become increasingly effective for heavy deformations between 50 and 95%. Larger ingots and hot forging will provide material for cold swagging and wiredrawing to very high strain levels.

Principal Investigator: D. H. Avery (Engineering).

SECTION 3

Inorganic Glasses

Introduction

The research of the Inorganic Glasses Group is focused on understanding the structures, relaxation phenomena, and electronic states and properties of the three principal types of inorganic glasses; amorphous metallic glasses, amorphous semiconductors, and oxide glasses. These reports of this research in 1979-80 can be read using either the phenomena or the types of glass as the organizing feature. But, the central fact that emerges is that fundamental issues concerning the amorphous state in general are being addressed by studying the materials.

Both the properties of important materials and discoveries of phenomena are reported. Thus, for example, the existence of the magneto-optic effect in metallic glasses was demonstrated, ultrasonic attenuation and velocity changes of metallic glasses were found to differ by orders of magnitude from the predictions of the two-level-system tunneling theory (which is sufficient for insulating glasses), the existence of a mobility edge in disordered electronic systems has been addressed using a field theoretic model of interacting matrices, and it has been shown using instanton methods that a.c. conductivity from the localized states in the band tail of a disordered solid is given as $\sigma(\omega) \sim \omega^2 (\log \omega)^{d+1}$ (d is the space dimensionality) confirming Anderson, Halperin and Mott's predictions.

Moreover, the existence of non-linear composition dependence (pronounced minimum) of isothermal compressibility $(K_{T,0}(T_f))$ in mixed alkali pentasilicates was shown, strong spectroscopic evidence for the existence of intermediate range structures in B_2O_3 was educed from isotopic substitution studies, it was shown that the proposed pure metaborate compound does not exist in the $MgO\text{-}B_2O_3$ system, the distribution of transition metal ions in oxide glasses was studied by neighboring atom nuclear spin relaxation, the role of a third component in enabling glass-formation in a ternary system whose binary components crystallize was studied, and measurements of dielectric loss at VHF to gigahertz frequencies on mixed alkali silicate glasses by time-domain methods showed that they exhibit previously unknown composition-dependent relaxations in this range.

In addition, the relaxation of photoinduced carriers in α-Si:H was studied and shown to be much slower than in α-Si or chalcogenide glasses and to be due to diffusion—limited bimolecular recombination. The dependence of the photoinduced absorption constant for silicon-rich alloys $(Si_{1-x}Ge_x)$ and α-Si:H was determined. It was interpreted on the basis of a model in which the photoinduced absorption band is due to transitions of holes from trap states close to the valence band into the valence band itself—a model which should permit using the picosecond absorption band to obtain information about hole traps in α-Si:H and related materials.

SECTION 3

Inorganic Glasses

Individual Contributions

Optical and Magneto-Optical Properties of Metallic Glass $Fe_{80}B_{20}$

We measured the optical constants of ferromagnetic $Fe_{80}B_{20}$ glass and the magneto-optic Kerr effect (MOKE). The optical absorption in the glass is compared to that of Fe and a shift of the structures in the $Fe_{80}B_{20}$ spectrum towards lower energies is noted. The MOKE absorption spectrum is similar in shape but reduced by a factor of about five compared to Fe. This exploratory work was done to find out whether the magneto-optic effect exists in metallic glasses. We found that it does exist and is measurable; however, the interpretation of the spectrum was difficult because of the complexity of the band structure of Fe. It was proposed that studies of this effect in amorphous materials with simpler electronic structures may be more informative (for example, on materials containing Ni instead of Fe; unfortunately these materials are much poorer glass formers).

Principal Investigator: J. Tauc (Engineering and Physics).

Personnel: L. Bieman (Engineering) and S. Ray (Physics).

Publication: "Optical and Magneto-Optical Properties of Metallic Glass $Fe_{80}B_{20}$," S. Ray and J. Tauc, Solid State Comm. *34* (1980), 769.

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

Ultrasonic Studies of Metallic Glasses

The results of thermal and ultrasonic studies of insulating glasses at low temperatures conducted over the past few years are generally found to be consistent with the predictions of the two-level-system (TLS) tunneling theory. The behavior of metallic glasses at low temperatures is less clear. Therefore, measurements of ultrasonic attenuation and velocity changes were carried out on the metallic glass $Pd_{0.775}Si_{0.165}Cu_{0.06}$ as a function of amplitude, in the frequency range 10 to 90 MHz, for $0.3 \leq T \leq 10$ K. A comparison of the experimental results with the predictions of the current two-level-system (TLS) tunneling theory is presented. The amplitude-dependent attenuation changes observed in these studies are larger by a factor of 100 to 1000 than the values obtained from current TLS theory, with the use of parameters determined experimentally at higher frequencies by other workers. Below ~ 1 K these attenuation changes have a linear (rather than quadratic) dependence on frequency and very weak temperature dependence (rather than $1/T$). The saturated (amplitude-independent) attenuation was found to have a very weak temperature dependence, rather than T^3 dependence. A significant amplitude dependence of the slope of the sound velocity change as a function of $\ln T$ was also observed.

Principal Investigator: C. Elbaum (Physics and Applied Mathematics).

Personnel: A. Hikata (Applied Mathematics), H. Araki (Materials Research Laboratory), and G. Park (Physics).

Publications: "Ultrasonic Studies of Amorphous PdSiCu," H. Araki, G. Park, A. Hikata, and C. Elbaum, Solid State Comm. *32* (1979), 625.

"Ultrasonic Studies of Metallic Glasses," H. Araki, G. Park, A. Hikata, and C. Elbaum, Proceedings of the International Conference on Phonon Scattering in Condensed Matter, ed. H. J. Maris (Plenum, 1980), p. 69.

"Ultrasonic Attenuation and Velocity Studies of Amorphous PdSiCu at Low Temperatures," H. Araki, G. Park, A. Hikata, and C. Elbaum, Phys. Rev. *B21* (1980), 4470.

Instantons and Disordered Systems

We have continued our work on disordered systems. It has been shown using instanton methods (publication 1) that a.c. conductivity from the localized states in the band tail of a disordered solid is given as $\sigma(\omega) \sim \omega^2 (\log \omega)^{d+1}$, d is the space dimensionality, confirming the predictions of Anderson, Halperin and Mott. The existence of a mobility edge in disordered electronic systems has been discussed using a field theoretic model of interacting matrices (publications 5 and 10). It is shown rigorously that all states are localized in two dimensions, above two dimensions for weak disorder there are mobility edges, but these merge above a critical amount of disorder and all states become localized.

We have also studied topological order in two dimensions. A field theory of dislocation mediated melting in two dimensions has been developed, a coupled vector sine Gordon theory. Thus we may now study this transition systematically (publication 8). The effect of a random symmetry breaking field on topological disorder in two dimensional systems has been studied. Such a field would simulate the interaction of the idealized two dimensional system with an underlying substrate if the substrate were to contain patches (islands) in which short range order is retained rather than being a single crystalline surface, e.g., charge density waves in chemisorption and physisorption. Planar model behavior should be observable for hexagonal perturbations (publication 7). In related work we have shown that the ratio of any two correction to scaling amplitudes is universal and have calculated the ratios to second order in $\epsilon = 4$-d. Agreement with experiment when available is excellent (publications 2, 3, and 9).

In the area of surface magnetism, the magnetization shape function at a free surface has been calculated explicitly using renormalized perturbation theory. To leading order

$$M(z) = t^\beta (6/g)^{1/2} c\phi(y)$$

$$\phi(y) = y^\sigma, \sigma = 1 - \epsilon/6$$

Here β is the bulk magnetization critical exponent (publication 6). We have also derived explicitly, using instanton methods, the form of the essential singularity at the coexistence curve in an Ising ferromagnet (publication 4).

Principal Investigator: A. Houghton (Physics).

Personnel: M-C. Chang (Physics).

Publications: "Two Particle Spectral Function and a.c. Conductivity of an Amorphous System Far Below the Mobility Edge: A Calculation of Interacting Instantons," A. Houghton, L. Schafer, and F. J. Wegner, Phys. Rev. B 22 (1980), 3598.

"Critical Amplitude Ratio of the Confluent Singular Term for the Specific Heat: Calculations to Order ϵ^2 for Systems of Continuous Symmetry," A. Houghton and M-C. Change, Phys. Rev. B 21 (1980), 1881.

"Universal Ratios Among Correction to Scaling Amplitudes on the Coexistence Curve," A. Houghton and M-C. Chang, Phys. Rev. Lett. 44 (1980), 785.

"The Metastable Ising Magnet in a Negative Field," A. Houghton and T. C. Lubensky, Phys. Lett. 77A (1980), 479.

"Noncompact σ Models and the Existence of a Mobility Edge in Disordered Electronic Systems Near Two Dimensions," A. Houghton, A. Jevicki, R. D. Kenway, and A. M. Pruisken, Phys. Rev. Lett. 45, (1980), 394.

"Singularities of the Surface Magnetisation Profile near the Critical Point," A. Houghton, D. R. Grempel, and S. C. Ying, Phys. Lett. A 78, (1980), 295.

"The Effects of a Random Symmetry Breaking Field on Topological Order in Two Dimensions," A. Houghton, R. D. Kenway, and S. C. Ying, Phys. Rev. B 23, (1981), 289.

"A Field Theory of Dislocation Mediated Melting in Two Dimensions," A. Houghton and M. C. Ogilvie, J. Phys. A L499-L454 (1980).

"Correction to Scaling Amplitude Ratios for the Superfluid Transition in ^{4}He," A. Houghton and M-C. Chang. Phys. Rev. B to be published.

"Noncompact σ Models and the Existence of a Mobility Edge in Disordered Electronic Systems near Two Dimensions," A. Houghton, A. Jevicki, R. D. Kenway, and A. M. Pruisken, Proceedings of the International Conference on Statistical Mechanics, Edmonton, Alberta, Canada, 1980.

Time Resolved Spectroscopy of Amorphous Semiconductors

We continued to work on the relaxation of photoinduced absorption in amorphous semiconductors. In the previous study we found that in non-hydrogenated amorphous silicon and chalcogenide glasses the photogenerated carriers decay very fast (on a picosecond scale) but in hydrogenated amorphous silicon (a-Si:H) the decay was much longer (exceeding the maximum time of 150 psec measurable with our picosecond equipment). Recently we studied the decay in a-Si:H in the time-range of 0.5 usec to 10 msec and found that the decay can be described as due to diffusion limited bimolecular recombination. The diffusion constant depends on time as $1/t^{1-\alpha}$; the parameter α (<1) was found to be between 0.6 to 0.7 in sputtered a-Si:H while in glow-discharge a-Si:H it varied with temperature. With our model for the photoinduced absorption band obtained from steady state studies, the decay data can be used to get information about the transport of electrons (more mobile carriers) which recombine with trapped holes. The time dependence of the diffusion constant points out the dispersive character of the transport, as observed also in other experiments on these materials, and is interpreted on the basis of the continuous-random-walk theory.

Principal Investigator: J. Tauc (Engineering and Physics).

Personnel: Z. Vardeny (Engineering) and S. Ray (Physics).

Publications: "Picosecond Relaxations in Amorphous Semiconductors," D. E. Ackley, J. Tauc, and W. Paul, J. Noncrystalline Solids *35 & 36*, (1980), 957.

"Optical Studies of Excess Carrier Recombination in a-Si:H: Evidence for Dispersive Diffusion," Z. Vardeny, P. O'Connor, S. Ray, and J. Tauc, Phys. Rev. Lett. *44*, (1980), 1267.

Photoinduced Optical Absorption in Amorphous Hydrogenated Silicon

We observed an infrared absorption band below the absorption edge induced by illumination in the fundamental absorption band in hydrogenated amorphous tetrahedrally bonded semiconductors, as reported previously. In a-Ge:H it was plausible to ascribe this band to photoinduced polaron hopping but in a-Si:H the spectrum could not be interpreted in this way. Recently we found that in a-Si:H and silicon rich a-Si$_{1-x}$Ge$_x$ alloys the photoinduced absorption constant $\Delta\alpha \sim (\hbar\omega - E_o)^{1/2}/\hbar\omega$ suggesting transitions from a state with a relatively sharply defined energy to a band with the square root density of electronic states. We proposed a model in which the photoinduced absorption band is ascribed to transitions of holes from trap states close to the valence band into the valence band. Using this model, study of the picosecond absorption band can be used to obtain information about the hole traps in a-Si:H and related materials.

Principal Investigator: J. Tauc (Engineering and Physics).

Personnel: P. O'Connor (Physics).

Composition Dependence of Isothermal Compressibility in Mixed Alkali Glass Forming Systems

In connection with our experimental and theoretical efforts to understand the mixed alkali effects on a range of properties, especially as they appear in dynamic mechanical properties, we have sought to relate the composition dependence of the properties of the glass-forming systems at their state at the fictive temperature, T_f, to those of the glasses themselves. Glasses in the series $xCs_2O(1-x)Na_2O \cdot 5SiO_2$ were studied and a novel and significant result was obtained in the variation of the low frequency bulk modulus at T_f with composition, i.e., $K_{T,0}(T_f)(x)$. It was found that $K_{T,0}(T_f)$ has a pronounced minimum with respect to x. This conclusion was made possible because our measurements also show that η^2 varies monotonically with x, so that $(\partial \epsilon / \partial C)_{P,T}$ changes slowly with x, and that T_g varies slowly with x, so the isothermal compressibility can be calculated assuming that density variations primarily affect light scattering intensity ratios. The fact that $K_{T,0}(T_f)$ varies non-linearly with x allows us to pose the question of whether this property of the materials at T_f is relevant to those of the glasses which, although they are in a different state below T_f, are the material actually measured and must retain the physical evidence of the T_f properties in some form. The hypothesis is that they do in the form of spatial variations in strain state, which manifest themselves in the response of the glasses to mechanical stresses in dynamic mechanical experiments and the mixed alkali effect on low frequency mechanical loss.

Principal Investigator: W. M. Risen, Jr. (Chemistry).

Personnel: E. I. Kamitsos (Chemistry).

Isotopic Study of Structure in Borate Glasses

The basic question about the structure of oxide glasses concerns the randomness of the systems. This question has been joined at the level of intermediate range order, since short range order follows chemical bonding principles in them and they are disordered over long ranges in the absence of orienting stresses. While special intermediate range structures have been identified spectroscopically in our work on arsenatophosphates, the continuous random network (CRN) approach holds that the spectra and properties of bulk-quenched glasses are consistent with random connections and orientations of all possible types. This issue is central to the structure of B_2O_3(gl), since the CRN approach has been proposed as the best way to treat the X-ray distribution function while all previous spectral work had led to the proposition that intermediate range structures—boroxyl rings—are the dominant features.

In this work the B_2O_3 glass system was prepared in the isotopic forms Pure $B_2O_3^{18}$ (gl), pure $B_2O_3^{16}$ (gl), and, by several routes, 0.5 $B_2O_3^{16}$, 0.5 $B_2O_3^{18}$ (gl), and their Raman spectra obtained and analyzed. Since the principal features in such spectra arise from symmetric modes based on B-O stretches, it is possible to distinguish between a boroxyl ring-based structure and a CRN structure. The CRN predicts that the principal mode arises from the density of states as a collective mode which would shift as one band with a frequency given by the average oxygen mass in the network. The boroxyl ring-based structure would lead to four bands, in the intensity ratio 1:3:3:1, for the 50% $B_2O_3^{16}$, 50% $B_2O_3^{18}$ glass, with the bands giving rise to the relative intensity of 1 being at the positions seen for the pure isotopic glasses. That was observed. The glass is composed nearly completely of boroxyl rings, and any CRN character must apply only to the connections between these large structures.

average oxygen mass in the network. The boroxyl ring-based structure would lead to four bands, in the intensity ratio 1:3:3:1, for the 50% $B_2O_3^{16}$ 50% $B_2O_3^{18}$ glass, with the bands giving rise to the relative intensity of 1 being at the positions seen for the pure isotopic glasses. That was observed. The glass is composed nearly completely of boroxyl rings, and any CRN character must apply only to the connections between these large structures.

Principal Investigator: W. M. Risen, Jr. (Chemistry).

Personnel: C. H. Windisch (Chemistry).

Publications: "Raman Study of Oxygen-labelled B_2O_3 Glasses," W. M. Risen, Jr. and C. H. Windisch, J. Noncrystalline Solids, 1981, in press.

"Spectra and Structure of Isotopically Labelled Alkali Borate Glasses," W. M. Risen, Jr. and C. H. Windisch, J. Noncrystalline Solids, to be submitted.

Supported by the Materials Research Laboratory/NSF and the Office of Naval Research.

Nuclear Magnetic Resonance Studies of Iron Lead Borate Glasses

Oxide glasses containing greater than 3 Mol % Fe_2O_3 are generally superparamagnetic or ferromagnetic making the observation of nuclear magnetic resonance (NMR) for the nuclei of non-magnetic atoms in these glasses impossible. However, glasses containing as much as 40 Mol % Fe_2O_3 which remain paramagnetic can be produced in the system $xFe_2O_3 - (1-x)[PbO \cdot 3B_2O_3]$. Hence, this system is ideal for studying B^{11} and Pb^{207} NMR in an iron-rich glass.

The linewidth of the narrow response of the B^{11} NMR spectrum has been obtained as a function of composition and applied field. These data are in good agreement with a model in which the iron-ions are randomly distributed in the glass matrix. In addition, computer simulations of the B^{11} and Pb^{207} NMR lineshape have been compared with the experimental spectra to derive values of B^{11} quadrupole interaction parameters, ratios of 4-coordinated to 3-coordinated atoms, and Pb^{207} chemical shift interaction parameters as a function of composition.

Principal Investigator: P. J. Bray (Physics).

Personnel: See below (Organic Solids).

Publications: See below (Organic Solids).

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

O^{17} and H^1 NMR Studies of SiO_2

SiO_2 enriched to 50% O^{17} has been fabricated in conjunction with Professor William Risen and his students in the Department of Chemistry. O^{17} and H^1 NMR spectra of the resulting amorphous powder have been obtained. The O^{17} spectrum exhibits sharply defined structure. The H^1 spectrum indicates protons are present in a concentration of approximately 10^2 ppm, and they are not present as interstitial water molecules but probably exist as hydroxyl groups in the glass.

Principal Investigator: P. J. Bray (Physics).

Personnel: See below (Organic Solids).

Publications: See below (Organic Solids).

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

NMR Studies of Glasses and Polycrystalline Materials in the ZnO - B_2O_3 System

The B^{11} NMR spectra for zinc borate compounds were secured and analyzed to identify the boron-oxygen structural groupings present in these materials. Results for polycrystalline materials at the 3:1 and 4:3 compositions (zinc oxide to boron oxide) were found to be indicative of boron-oxygen groupings which correlate with structures proposed in the literature. A third compound at the diborate (1:2) composition is currently under investigation.

Zinc borate glasses were made and studied. The NMR spectra were found to be very similar throughout the range of glass formation. This indicates that a similarity in structure exists between all the glasses in this system. The fraction of boron in four-coordination, N_4, was determined for each of the glasses. A consistent difference in N_4 was found for glasses having the same compositions with different thermal histories.

Principal Investigator: P. J. Bray (Physics).

Personnel: See below (Organic Solids).

Publications: See below (Organic Solids).

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

The Structures of Compounds and Glasses in the System MgO - B_2O_3 Using B^{11} NMR

Structural groupings in the system MgO - B_2O_3 were studied by the technique of computer fitting B^{11} NMR experimental lineshapes. The results are strongly dependent on sample preparation and indicate that the pure metaborate compound does not exist. Previous models of the structure of glasses in this system must be reexamined in light of these findings.

Principal Investigator: P. J. Bray (Physics).

Personnel: See below (Organic Solids).

Publications: See below (Organic Solids).

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

Tellurium Borate Glasses

Tellurium borate glasses containing either lithium oxide or aluminum oxide as third components have been made and studied using NMR. The binary tellurium borate system was found to have a large region of immiscibility. However, homogeneous glasses could be made through the addition of lithium oxide or alumina. The B^{11} NMR spectra for glasses in the above systems were secured and used to study the behavior of N_4, the fraction of boron atoms in four-coordination. The N_4 results indicate that the TeO_2 in the glasses contributes to the formation of four-coordinated boron atoms. There is an apparent change in the coordination of tellurium atoms from four to three with the subsequent release of oxygen atoms. The Te^{125} spectra in these glasses are under investigation and will aid in understanding both the behavior of tellurium and boron in these materials.

Principal Investigator: P. J. Bray (Physics).

Personnel: See below (Organic Solids).

Publications: See below (Organic Solids).

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

Time Domain Spectroscopy and Dielectric Properties of Glassy Materials

Preliminary measurements of several mixed alkali glasses made by W. M. Risen's research group have indicated small but definite losses at VHF to gigahertz frequencies which are composition dependent and in excess of ordinary conduction effects. Work in progress is directed at better definition of these losses after further refinement of time domain difference methods previously developed in this laboratory.

A program in collaboration with G. T. Evans (Oregon State) was started to test his Brownian dynamics calculations of kinetics of polymer chain configurational changes. These can be probed by dielectric relaxation of electric dipole orientations, and there are intriguing indications that a basis for molecular understanding of the "skewed-arc" relaxation function found for many solid materials may be at hand, at least for linear chain polymers.

Related work, with support primarily from other sources, was a series of measurements of ion-dipole interaction effects in a series of electrolyte solutions as a further test of Hubbard-Onsager and Wolynes-Hubbard theories of kinetic depolarization. This until recently unrecognized effect was confirmed by our measurements of sulfuric acid, and is now believed to have a significant bearing on ionic mobilities in a variety of systems.

Considerable time was spent preparing two review manuscripts for publication: one on dipole correlation function theories of dielectric relaxation in solids (for a British Institute of Physics symposium), and the other on Fourier transform methods for study of dielectric polarization (as part of an ACS symposium volume).

Principal Investigator: R. H. Cole (Chemistry).

Publication: "Evaluation of Dielectric Behavior by Time Domain Spectroscopy. 3. Precision Difference Methods," R. H. Cole, S. Mashimo, P. Winsor, IV, J. Phys. Chem. *84* (1980), 786.

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

Organic Solids

Both N^{14} and Cl^{35} NQR data have been obtained for a series of compounds containing nitrogen directly bonded to chlorine. The existence of an inverse correlation between the N^{14} and Cl^{35} quadrupole coupling constants is interpreted in terms of a simple model dealing with charge excesses and deficiencies at the respective nuclei. The relationship between the ionic character of the N-Cl bond and the NQR data is discussed, and the possibility of obtaining a value for the atomic quadrupole coupling constant of N^{14} (e^2q_pQ) is noted. The Townes and Dailey method of computing electron charge densities from the NQR frequencies is shown to be satisfactory in giving consistent results, provided that the hybridization of the nitrogen orbitals is known.

The ^{14}N NQR spectra of 22 monosubstituted anilines have been obtained and analyzed in the framework of the Townes and Dailey theory. Satisfactory correlation of the NQR data with both the Hammett σ parameters and the *in vitro* biological activities of the corresponding sulfanilimides have been found. The results obtained suggest that the nitrogen lone-pair orbital is more sensitive than the nitrogen-carbon sigma orbital is to substituent effects.

^{14}N NQR spectra have been obtained at 77°K for several organic dye cations and one free base. The cations are weakly paramagnetic at 77°K exhibiting broad and featureless ESR spectra characteristic of weak charge-transfer complexes. The positive charge in the cations is largely delocalized. The existence of a simple relationship between the ^{14}N NQR data and optical properties for three cyanine laser dyes has been studied.

^{14}N NQR spectra have been obtained for a series of monomeric carbazole compounds including N-vinyl carbazole, which in the polymeric form of this compound is one of the most sensitive photoconductive organic polymers. Electron distributions determined from the NQR data show clearly and quantitatively the delocalization of pi electrons in carbazole as compared to pyrrole. Effects of substituents such as aldehyde and vinyl groups on the molecular charge distributions have been studied.

Principal Investigator: P. J. Bray (Physics).

Personnel: F. Bucholtz (Physics), W. J. Dell (Physics), A. E. Geissburger (Physics), I. A. Harris (Physics),

S. G. Greenbaum (Physics), M. Lui (Physics), and M. L. Buess (Physics).

Publications: "B^{11} NMR Studies of the Structure of Borate Glasses," P. J. Bray, S. A. Feller, G. E. Jellison, Jr., and Y. H. Yun, J. Non-Crystalline Solids, *38 & 39* (1980), 93-98.

"Si^{29} NMR Spectra of Glasses and Polycrystalline Compounds in the System K_2O-SiO_2," I. A. Harris, Jr. and P. J. Bray, Phys. and Chem. of Glasses *21*, (1980), 156.

"B^{11} Nuclear Magnetic Resonance Studies of Li_2O-B_2O_3 Glasses at High Li_2O Content," Y. H. Yun and P. J. Bray, submitted to J. Non-Crystalline Solids.

"The Use of Magnetic Fields for ^{14}N NQR Spin-Echo Signal Enhancement," M. L. Buess and P. J. Bray, accepted for publication in the J. Mag. Res.

"N^{14} Nuclear Quadrupole Resonance in Carbazoles," N. S. Kim and P. J. Bray, submitted to J. Organic Magnetic Resonance.

"B^{11} NMR Studies of Glasses in the System $xFe_2O_3(1-x)[PbO \cdot 3B_2O_3]$," F. Bucholtz and P. J. Bray, Am. Cer. Soc. Bull. *59*, (1980), 863.

"Investigation of Nitrogen-Chlorine Bonds by ^{14}N and ^{35}Cl NQR," S. G. Greenbaum and P. J. Bray, Bull. Am. Phys. Soc., 25(1980), 272.

"^{14}N Nuclear Quadrupole Resonance Study of Substituted Anilines and Prediction of in vitro Activity of Sulfanilamides," S. G. Greenbaum, S. N. Subbarao, P. J. Bray, and T. Oja, J. Organic Magnetic Resonance *14*(1980), 379.

"^{14}N Nuclear Quadrupole Resonance in Weakly Paramagnetic Organic Dye Cations," S. G. Greenbaum and P. J. Bray, submitted to J. Magnetic Resonance.

"The Determination of the Structures of Compounds and Glasses in the System MgO-B_2O_3 Using B^{11} NMR," M. J. Park, K. S. Kim, and P. J. Bray, Phys. Chem. Glasses *20*,(1979), 31.

SECTION 4

Chemisorption and Related Surface Interactions

Introduction

The work in this thrust area is concerned with the basic properties of solid surfaces and with the fundamental interactions occurring in chemisorption processes and surface reactions. The experimental studies cover a range of model substrates, from well-defined single-crystal surfaces to metal clusters on certain polymers. The theoretical work extends from a simple jellium picture to more realistic models of alkali and transition metals.

Static surface properties, such as crystallographic and electronic structure, have been investigated experimentally by Estrup and Stiles, using low energy electron diffraction (LEED), surface reflectance spectroscopy (SRS), photoelectron spectroscopy (UPS, XPS), and other methods. At the same time, Ying has carried out theoretical work on the electronic and magnetic properties of metal surfaces, and has considered the effects of surface defects. Several studies are underway concerning phase diagrams and surface phase transitions; this work is likely to receive increasing emphasis and will involve a particularly close collaboration between experimentalists and theorists.

Studies of dynamic surface properties include investigations, by Greene, of the scattering and ionization of atomic beams; and the laser-spectroscopic investigations, by Diebold, of collisional energy transfer to diatomic molecules. In addition, Estrup has studied the kinetics of dissociation and desorption of simple molecules on metal surfaces; and Risen has investigated the reaction of similar species on metals supported in ionomers.

SECTION 4

Chemisorption and Related Surface Interactions

Individual Contributions

Experimental Studies of Chemisorption

Studies of surface structure and surface kinetics have been carried out on well-defined systems consisting of chemisorbed layers on single crystals of molybdenum and tungsten.

The nature of the reconstructed Mo(001) and W(001) surfaces has been investigated by LEED and associated techniques. On the clean substrates, at low temperature, the surface atoms are found to be displaced along the ‹11› directions but adsorption of hydrogen (and probably other adsorbates) causes a shift to the ‹10› directions. Evidence has been obtained indicating that the surface phases result from a periodically varying adatom occupation probability coupled to the displacement waves. Data for hydrogen desorption suggest that the substrate rearrangement is the major cause of the observed coverage dependence of the adsorbate properties. Similarly, studies by photoelectron spectroscopy of the kinetics of CO dissociation on Mo(001) show that the rate behavior can be explained by an activation energy which increases at the same coverage at which the substrate changes structure.

In collaboration with P. J. Stiles (see below), surface reflectance studies have been made of chemisorbed layers on the W(110) surface. Information about adsorbate bonding and about surface phase transition has been obtained by this technique.

Principal Investigator: P. J. Estrup (Physics and Chemistry).

Personnel: R. A. Barker (Chemistry), R. Robertshaw (Physics), and S. Semancik (Physics).

Publications: "Simple DC Method for the Continuous Measurement of Work Function Changes," P. J. Estrup, R. A. Barker, T. E. Felter, and S. Semancik, J. Vac. Sci. Technol. *17* (1980), 755.

"Surface-Reflectance-Spectroscopy Studies of H on W(110): Surface Band Structure and Adsorbate Geometry," P. J. Estrup, G. Blanchet, and P. J. Stiles, Phys. Rev. Lett. *44* (1980), 171.

"Atomic Displacements on the Mo(001) and H/Mo(001) Surfaces," P. J. Estrup, R. A. Barker, and S. Semancik, Surface Sci. *94* (1980), L162.

"Photoemission Method for the Study of Surface Kinetics: CO on Mo(100)," P. J. Estrup and S. Semancik, J. Vac. Sci. Technol. *17* (1980), 233.

"Substrate Rearrangement and 2D Ordering," P. J. Estrup, in *Ordering in Two Dimensions*, S. Sinha, ed. (North-Holland) 39 (1980).

Supported by the Materials Research Laboratory/NSF.

Surface Reflectance Spectroscopy

It has been found that surface reflectance spectroscopy (SRS) is a powerful tool for the study of surface electronic structure and bonding. By including reflectance measurements at different angles of polarization, we have obtained information not only about the band structure but also about the geometry of the adsorbate complex. Recent work has shown, furthermore, that surface phase transitions give rise to characteristic reflectance changes, and SRS has been employed to map the two-dimensional phase diagram (in the temperature-coverage

plane) for the O/W(110) chemisorption system.

Principal Investigator: P. J. Stiles (Physics).

Personnel: G. Blanchet (Physics) and B. Parker (Physics).

Publications: "Chemisorption-Induced Changes of the Surface Dielectric Function for W(110)," P. J. Stiles and G. Blanchet, Phys. Rev. *B21* (1980), 3273.

"Surface-Reflectance-Spectroscopy Studies of H on W(110); Surface Band Structure and Adsorbate Geometry," P. J. Stiles, G. Blanchet, and P. J. Estrup, Phys. Rev. Lett. *44* (1980), 171.

Supported by the Materials Research Laboratory/NSF.

Phase Transitions in Chemisorbed Systems

We have developed a statistical mechanical model for the structural phase transitions observed on many metal surfaces. The effect of adsorbates on this transition is studied in detail. Depending on the coverage and temperature, the adsorbate can either suppress, enhance or change the transition from a commensurate order into an incommensurate one. Thus the chemisorbed metallic surface provides a unique and rich system for the study of structural phase transitions. In the case of incommensurate order, one can obtain a physical realization of the X-Y model. The effect of random impurities on the topological order in this case has been investigated via field theoretical methods.

Principal Investigator: S. C. Ying (Physics).

Personnel: K. H. Lau (Physics).

Publications: "Effect of H-Adsorption on the Displacive Transition of W(001) Surface," K. H. Lau and S. C. Ying, Phys. Rev. Lett. *44* (1980), 1222.

"Hydrogen Chemisorption and the Displacive Transition of W(100) Surface," K. H. Lau and S. C. Ying, in *Ordering in Two Dimensions*, North Holland (1980).

"Effect of Substrate Distortion on the Ordered Phases in Chemisorption Systems," S. C. Ying, invited talk delivered at the 27th National Symposium of A.V.S. (1980) and published in Journal of Vacuum Science and Technology.

"Effect of a Random Symmetry-Breaking Field on the Topological Order in Two Dimensions," A. Houghton, R. D. Kenway, and S. C. Ying, Phys. Rev. B *23* (1981), 289.

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

Electronic Structure of Defects and Surfaces in Simple Metals

The density matrix variational method has been applied to the study of low index surfaces of alkali metals. The three-dimensional electronic density and surface potential are obtained for the first time for the entire series of alkali metals. They differ significantly from the corresponding results of the widely used jellium model.

A corresponding study has been made for a monovacancy in Na. The discrete lattice nature is found to change the Friedel oscillations around the vacancy significantly from the jellium picture.

Principal Investigator: S. C. Ying (Physics).

Personnel: K. P. Bohnen (Physics) and M. Lega (Physics).

Magnetic Properties of Surfaces

We have developed a new method for calculating the Green's functions for a tight binding Hamiltonian. This method was applied to the study of the magnetic properties of surfaces of Ni, V and Cr. Substantial surface enhancement is found for both V and Cr, in agreement with recent experimental findings. By including the contribution of spin fluctuations, we have also accounted satisfactorily for the transition temperature and the Curie-Weiss like susceptibility of these systems at finite temperatures.

In addition, we have investigated the surface magnetization profile of an Ising type magnet near the critical temperature.

Principal Investigator: S. C. Ying (Physics).

Personnel: D. R. Grempel (Physics).

The Scattering and Ionization of Atoms at Surfaces

The first part of the study of the efficiency with which atoms are ionized on surfaces is nearly complete. Atomic beams of K, Na, Li, and Tl have been directed at surfaces of Pt and Si, and the variation of the yields of scattered ions with temperature has been measured. The results show that the statistical ratio of ions to atoms leaving the surface is found except for some special cases. These deviations lead to conclusions about the state of the surface. Analysis of the composition of the surface by Auger spectroscopy can be done between the ionization measurements to check for the presence of impurities. Preliminary measurements on an insulator, Al_2O_3, suggest that the statistical ratio is no longer produced, so the analysis of results will be able to give information on kinetic as well as equilibrium processes.

The apparatus originally chosen for measurements of the elastic scattering of rare gases from the surfaces of crystals of graphite has been shown to be unsuitable for the purpose. The lack of enough differential pumping and the relatively high ultimate pressure were the main problems. A new apparatus has been designed, the components have been built, and the assembly is now being finished. The angular distributions of elastically scattered atoms, that the new apparatus should yield, promise to give useful information about the structure of the surface.

Principal Investigator: E. F. Greene (Chemistry).

Personnel: A. LeGrand (Physics), J. Keeley (Chemistry), and M. Pickering (Chemistry).

Inelastic Scattering of Diatomic Molecules from Solid Surfaces

As noted in our last report, the presence of scattered molecules in the target chamber has increased the problem of background interference so that we are unable to distinguish between background absorption and absorption from the scattered beam. We are at present developing pulsed beam sources so that we can eventually eliminate this problem. In the interim we have been investigating a new tool for scattering studies. We have investigated a new universal detector that can serve as a beam detector in studies of gas-solid scattering. This device should be particularly suitable for use with the pulsed valve now on order, although it will function when an amplitude modulated, continuous beam is used.

Principal Investigator: G. J. Diebold (Chemistry).

Personnel: J. Hayden (Chemistry).

Publication: "Direct Detection of Momentum Flux in Atomic and Molecular Beams," J. G. Choi, J. Hayden, M. O'Connor, and G. J. Diebold, to be published.

Surface Complex Models on Rh-PFSA Ionomers

The studies of reactions of small molecules with metal ions supported in PFSA ionomers are designed to help elucidate the structure and bonding of chemisorbed species on metals and supported metals. Our recent work with Rh-PFSA has established a clear connection between these systems and those known to be catalytically active. Chemisorption of CO on Rh supported by Al_2O_3 or SiO_2, for example, is a widely studied step in the processes catalyzed by supported Rh. A range of vibrational bands for such sorbed CO molecules typically is observed and assigned to CO on metallic Rh. Our work on Rh-PFSA reacted with CO or CO/H_2 shows, however, that while all of the features seen on the active catalysts are observed in this system (as well as another for weakly chemisorbed CO on Rh(III)), most of the previous interpretations must be changed. The two strong features commonly seen with CO on $Rh(Al_2O_3)$ are not due to CO on Rh(O) at all, but are due to oxidized rhodium (Rh(I)), and two higher frequency features are due to CO on Rh(III) sites. The lower frequency (ca 1850-1930 cm^{-1}) features for CO on dispersed-Rh catalysts are not due to a distribution of bridging CO structures alone, but to a distribution of them and of Rh oxidation states. Finally, those features which are characteristic of CO on Rh(O) centers are observed in Rh-PFSA. Moreover, both the high temperature (ca 300°K) and low temperature (ca 100-150°K) forms of CO on Rh(O) can be formed through different chemical routes with Rh-PFSA.

The work on this and related M-PFSA systems continues in order to model effectively and study chemisorption species on a variety of metals. Preparation in this way permits studies which are not possible on the catalysts themselves.

Principal Investigator: W. M. Risen, Jr. (Chemistry).

Personnel: D. M. Barnes (Chemistry).

Publication: "Reactions of Supported Rhodium Species with CO: Comparison of the Rh-PFSA System with Rh on Al_2O_3 or SiO_2," W. M. Risen, Jr. and D. M. Barnes, J. Catalysis, in submission, 1981.

SECTION 5

Lower Dimensional Systems

Pseudo One Dimensional Conductors

The effect of impurities and the coupling of several chains via phonons for quasi-one-dimensional systems has been considered. For the study of electron localization and delocalization (1), we considered the large momentum $(2k_f)$ scattering of the electrons by impurities in addition to the usual backward scattering interactions. This problem bears a very strong mathematical similarity to the case of coupling of several chains via phonons (2,3) (modulo the randomness of the impurities). For the latter problem, we consider BS model on each chain and the large momentum part of the electron-phonon coupling. Mandelstam operators (generalized to the case of several chains) are used to bosonize the two problems. The resulting theories are formally related to the SU(2) Massive Thirring model (on each chain) with the proper renormalizations. The mass gaps, the ranges in which they exist and thus the ranges of localization and delocalization are obtained by using a method developed earlier (4). We found that these ranges depend both on $2V-U_{11}$ and U_{11} in contrast to some other results (5). We also concluded that the transition (from the massless to the massive phases) has an XY-like behavior and that the problem is equivalent to two coupled Coulomb gases. Methods of calculation of the correlation and the free energy are discussed.

We found that the expression for the periodic boundary conditions (PBC) obtained in the diagonalization of 1D theories by the Bethe *Ansatz* method contains all the physics of the problem and that they can be used to relate and classify various one-dimensional and two-dimensional models (5). In addition to the exact spectrum, we obtain an infinite number of conserved charges, the S-Matrix, and various correlation functions. We are then able to take the continuum limit of lattice theories without any ambiguities. It is found that two different limits of the spin-1/2 XYZ chain leads the Bose-Gas and the Massive Thirring Model (6). In view of the results obtained in this investigation involving 1D and 2D models, it is concluded that for a given internal symmetry there is only one fundamental model and only one Bethe *Ansatz*. The others are obtained by various limits or transformations. We find for example that the "gauge" equivalence of some 1D models is realized as a mapping of the kernel and/or the inhomogeneous parts of these integral equations. These considerations allow the classification of one-dimensional or two-dimensional models.

REFERENCES

(1a)E. Berkcan and L. N Cooper, to be published.

(1b)E. Berkcan and L. N Cooper, submitted to "Physics in One-Dimension" (ed. by J. Bernasconi and T. Schneider).

(2)E. Berkcan and L. N Cooper, J. Less Com. Metals, *62* (1978), 349.

(3)V. S. Emery, Phys. Rev. Lett. *37* (1977), 107.

(4)E. Berkcan. L. N Cooper and B. Stolan, Phys. Rev. *B17* (1978), 3624.

(5a)S. T. Chui and J. W. Bray, Phys. Rev. *B16* (1977), 1329.

(5b)*Ibid. B19* (1979), 4020.

(6a)E. Berkcan, L. N Cooper and U. Mohanty, to be published.

(6b)E. Berkcan and L. N Cooper, submitted to "Physics in One-Dimension" (ed. by J. Bernasconi and T. Schneider).

(7)See also A. Luther, Phys. Rev. *B14* (1979), 2153.

Principal Investigator: L. N Cooper (Physics).

Personnel: E. Berkcan (Physics).

Publications: "Bethe *Ansatz,* Connection Between One-Dimensional Models and Their Classification," E. Berkcan and L. N Cooper, in press.

"Electron Localization vs. Delocalization and $2k_f$ vs. $4k_f$ Scattering Within the Backward Scattering Model: The Underlying Structure," E. Berkcan and L. N Cooper, to be submitted.

"The Bethe *Ansatz,* Periodic Boundary Conditions and Relations between Various Models," E. Berkcan, L. N Cooper and U. Mohanty, to be submitted.

Supported by the Materials Research Laboratory/NSF.

Surface Excitations In Conducting Solids

In conducting solids in which the electron density does not drop abruptly from its bulk value to zero at the surface, a new class of surface modes called "higher multipole excitations" can occur. We have investigated these modes for the case of a degenerate polar semiconductor with a surface depletion layer. The higher multipole excitations interact with the polar phonons giving rise to "multipolariton modes" of the surface depletion layer. The dispersion of these modes has been studied for a simple two-step model in the long wavelength non-retarded limit.

Principal Investigator: J. J. Quinn (Physics).

Personnel: K. S. Yi (Physics).

Publications: "A Simplified Treatment of Exchange and Correlation in Semiconducting Surface Inversion Layers," J. J. Quinn, R. K. Kalia, G. Kawamoto, and S. C. Ying, Solid State Comm. *34* (1980), 423.

"Surface Helicon Waves in the Faraday Geometry; Do They Exist," J. J. Quinn and P. Halevi, Solid State Comm. *33* (1980), 467.

"Theory of the Effect of a dc Current on Surface Polaritons in n-Type Silicon," J. J. Quinn, B. G. Martin and R. F. Wallis, to appear Surf. Science.

"Theory of the Effect of a dc Current, Including the Electron Thermal Pressure Gradient on Surface Polaritons in n-Type Silicon," J. J. Quinn, B. G. Martin, and R. F. Wallis, Proc. Int. Conf. on Surfaces and Thin Films, Cannes, 1980.

"Exchange-Correlation Effects in Silicon Inversion Layer: Valley Occupancy Phase Transitions," J. J. Quinn, W. L. Bloss, S. C. Ying, T. Cole, and B. D. McCombe, Proc. Int. Conf. on Semiconductor Physics, Kyoto, 1980.

"Exchange Correlation Effects in Silicon (111) Inversion Layers: Stress Enhanced Valley Occupancy Phase Transition," J. J. Quinn, W. L. Bloss, and S. C. Ying, to appear Phys. Rev.

"Magneto-Plasma Surface Waves of a Degenerate Semiconductor in the Faraday Geometry - Effect of the Presence of a Metallic Screen," J. J. Quinn, K. S. Yi, and P. Halevi, Phys. Rev. *22* (1980), 6247.

"Surface Modes of a Degenerate Polar Semiconductor with a Surface Depletion Layer," J. J. Quinn, S. Das Sarma, and A. Eguiluz, to appear Solid State Comm.

"Properties of a Surface Inversion Layer in a Polar Semiconductor," J. J. Quinn, G. Kawamoto, and W. L. Bloss, to appear Phys. Rev.

"Multipolaritons of a Polar Semiconductor Surface Depletion Layer," J. J. Quinn, S. Das Sarma, and A. Eguiluz, Proc. of Int. Conf. on Phys. of Compound Semiconductors, Williamsburg, 1981.

"Evidence for Valley Occupancy Phase Transition in Si-(100) Inversion Layers," J. J. Quinn, T. Cole, B. D. McCombe, and R. K. Kalia, submitted to Phys. Rev. Letters.

Low-Dimensional Quantum Field Theories and Their Application to Disordered Systems

We studied the zero temperature electrical conductivity of a disordered solid in $2 + \varepsilon$ dimensions. This is related to the critical behavior of a non-linear σ-model on the non-compact space $O(M,M)/O(M)xO(M)$ in the limit $M \to 0$. We calculated the β-function to one loop order for general Einstein spaces, deducing from it that all electronic states are localized in 2 dimensions. Above 2 dimensions, for weak disorder there are mobility edges, but these merge above a critical amount of disorder and all states become localized.

Guerin and Kenway formulated a strong-coupling expansion in the inverse fermion propagator for the N-species Gross-Neveu model, and summed it to all orders in the large-N limit. We recovered all the exact results previously derived from the weak-coupling expansion and were able to compare different regularization schemes.

Houghton, Ying, and Kenway looked at the effect of quenched random symmetry-breaking fields on topological order in the 2 dimensional XY model. This was to understand whether substrate impurities interfere with a Kosterlitz-Thouless phase transition in the absorbate. We used a renormalization group analysis of the equivalent sine-Gordon field theory to show that the transition survives provided the random field has locally three-fold symmetry or higher.

Principal Investigator: R. D. Kenway (Physics).

Personnel: A. Houghton (Physics), S. C. Ying (Physics), F. Guerin (Physics), A. Jevicki (Physics), and A. M. Pruisken (Physics).

Publications: "Non-Compact σ-Models and the Existence of a Mobility Edge in Disordered Electronic Systems Near Two Dimensions," A. Houghton, A. Jevicki, R. D. Kenway, and A. M. Pruisken, Phys. Rev. Lett. *45* (1980), 394.

"A Strong-Coupling Expansion for Fermion Field Theories and the Large-N Limit of the Gross-Neveu Model," F. Guerin and R. D. Kenway, Nucl. Phys. *B176* (1980), 168.

"The Effects of a Random Symmetry-Breaking Field on Topological Order in Two Dimensions," A. Houghton, R. D. Kenway, and S. C. Ying, Phys. Rev. *B23* (1981), 298.

Resonance Raman Spectra of Highly Conducting Poly-p-phenylene Complexes

The discovery of the highly conducting charge-transfer complexes of poly-p-phenylene has attracted a great deal of attention. Through chemical doping with electron-acceptors, such as AsF_5, or donors, such as Na, the electrical conductivity of these conjugated π-electron systems increases from insulating to metallic values $(1 \times 10^3 \text{ S m}^{-1})$. The major problem in studying such systems as these, polyacetylenes, or others is in discovering the nature of the polymer after doping—i.e., how its structure, electron states, etc. have been changed by doping. This is a problem because vibrational spectroscopic methods have not been successful previously in obtaining this information on the highly conducting forms.

In this work the resonance Raman spectra of poly-p-phenylene (PPP) and its highly conductive AsF_5- and Na-doped charge transfer complexes have been obtained and shown to reveal the effects on the polymer caused by doping. There is selective enhancement of different vibrational bands associated with the in-ring and bridge

bonds of the different samples. One key result is that doping with either type of dopant causes the C-C bond joining the phenyl rings to become stronger and at least one of the in-ring bonds to become weaker, so all C-C bonds along the backbone of the π-electron system become more alike than they are in the undoped PPP. Another is that the resonance enhancements show the relationship between changes in molecular configuration caused by optical transitions in the donor- or acceptor-doped PPP and the vibrational modes of the polymer. Finally, the data are analyzed in terms of the proposed electronic structures of pure and doped PPP.

Principal Investigator: W. M. Risen, Jr. (Chemistry).

Personnel: C. H. Tzinis (Chemistry) and E. I. Kamitsos (Chemistry).

Publication: "Raman Spectra of Highly Conducting Poly-p-phenylene Charge Transfer Complexes," W. M. Risen, Jr., C. H. Tzinis, and R. H. Baughman, Solid State Comm., in submission.

Supported by the Materials Research Laboratory/NSF and the Office of Naval Research.

Lower Dimensional Studies

This period involved the initiation of many new experiments. We have begun measurements to determine if the predicted 2-1 valley transition of Bloss and Quinn exists. We have determined new information on valley degeneracies in (110) and (111) surface MOSFET structures in Si. We see a transition from 6 valleys to 2 valleys in new (111) MOSFETs as well as just 2 valleys on other (111) MOSFET structures (prepared differently). We see 4 valleys on (110) surfaces on our newer samples. At sufficiently high magnetic fields, we see a transition to 1 valley structure.

We have indications that high pressure oxidation will lead to a better $Ge:GeO_x$ structure to study two-dimensional electron gases. Work continued on electrons on helium, but was unsuccessful. We are continuing that study and the plasma oxidation of GaAs.

Principal Investigator: P. J. Stiles (Physics).

Personnel: E. Crisman (Physics), C. Huber (Physics), J. Lee (Physics), K. C. Woo (Physics), and R. Zeller (Engineering).

Publication: "Quasi-Two-Dimensional Electrons in Surface Space Charge Layers," P. J. Stiles, to be published.

Supported by the Materials Research Laboratory/NSF, the National Science Foundation, and the Office of Naval Research.

SECTION 6

Low Temperature Properties of Materials

Study of Rotons In Liquid Helium-Four

The theory of roton second sound in superfluid helium-4 is considered. We first derive the hydrodynamic equations which determine the motion of a pure roton gas. The collisions between rotons are assumed to conserve energy, momentum, and the number of rotons. The hydrodynamic equations without dissipative terms have the same form as the corresponding equations for an ordinary fluid. When lowest order dissipative effects are included, it is found that there are some extra dissipative processes in addition to heat conduction and viscosity. We next consider modifications of the hydrodynamic equations which occur when the effects of collisions between rotons and phonon are included, and when there are some roton-roton collisions in which the roton number changes. It is found that at the temperatures and pressures where roton second sound has so far been observed, the wave motion is best described as isothermal second sound. We show that current experimental data indicate that in nearly all collisions between rotons (>99.97%) the total number of rotons is conserved.

Principal Investigator: H. J. Maris (Physics).

Personnel: R. W. Cline (Physics).

Publications: "Velocity of Roton Second Sound," R. W. Cline and H. J. Maris, in *Proceedings* of the Third International Conference on Phonon Scattering in Condensed Matter, ed. by H. J. Maris (Plenum, New York, 1980), p. 161.

"Roton Second Sound and Roton Scattering," R. W. Cline and H. J. Maris, to appear in Phys. Rev. B., April 1981.

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

Kapitza Resistance

We have carried out an experiment to measure the Kapitza resistance between liquid and solid helium, and have obtained some preliminary data. This experiment is important because the surface of solid helium is highly perfect and clean, and so one has the opportunity to study the Kapitza resistance in the absence of surface damage or dirt. We hope to make more measurements and analyze the data during the next few months.

Principal Investigator: H. J. Maris (Physics).

Personnel: T. E. Huber (Physics).

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

Energy-Selective Phonon Detector

We have continued our experimental study of phonon detection using superconducting zinc films. The characteristics of the detector have been explored by means of several experiments with phonons and rotons in superfluid helium. Measurements of the threshold energy for phonon detection, and its correlation to changes in the I-V characteristics with magnetic field have been made. A tentative explanation of the detection mechanism in terms of phonon-activated fluxoid motion has been proposed.

Principal Investigator: H. J. Maris (Physics).

Personnel: R. W. Cline (Physics).

ESR of Atomic Hydrogen at 4.2°K

ESR measurements at 9GHz have been performed on atomic hydrogen in a cavity the walls of which are coated with solid molecular hydrogen at low temperatures. At 4.2°K and below, a broad line spectrum is observed and ascribed to atoms trapped on the surface of solid H_2 at fixed sites. The broad line spectrum, which appears in addition to the narrow line spectrum associated H atoms in the gas, has several notable characteristics—a g shift, shift in hyperfine interaction and line width that are compatible with atoms in surface states. The absorption spectrum persists indefinitely below 4°K when the source of H atoms is turned off. And as the temperature is lowered, the broad spectrum increases in intensity as the narrow spectrum decreases. Furthermore, on turning off the source of H atoms and warming to 4.2°K, the broad spectrum is stronger than with the source on and the narrow gas resonance present.

We interpret these observations as indicating that the broad line spectrum originates from H atoms trapped at fixed sites on the surface of molecular H_2. Support for this contention comes from a comparison of the measured parameters of this spectrum with those found by other workers for H atoms incorporated in solid H_2, from the difficulty of others in creating atoms in solid H_2 by deposition, and from the dependence of the intensity of the broad line on the narrow line. Our measurements require a density of immobile surface states of between 10^{10} and $10^{11}/cm^2$, suggesting that the localized sites are limited to defects and grain boundaries on the surface.

Principal Investigator: G. M. Seidel (Physics).

Personnel: R. Mayer (Physics) and J. Cameron (Physics).

Recovery of Solid Helium-4 After Plastic Deformation

Recovery of both bcc and hcp phases of solid helium-4, after being subjected to plastic deformation, has been investigated by measuring attenuation changes as a function of time. Bcc and hcp He^4 show distinctly different behavior. In bcc He^4, the attenuation changes somewhat upon deformation and relaxes within a time of order of one minute. In hcp He^4, attenuation changes considerably upon deformation and it takes a time of order of 10 minutes to relax.

Principal Investigator: C. Elbaum (Physics and Applied Mathematics).

Personnel: H. Kwun (Materials Research Laboratory).

- 44 -

Finite Amplitude Wave Propagation in Solid and Liquid Helium-4

Amplitude response of a longitudinal ultrasonic wave (10MHz) was investigated in solid helium (bcc and hcp phases) as well as in liquid helium (normal and superfluid phases). The amplitude response curves show saturation behavior which is well described by an equation for amplitude loss based on second-harmonic generation.

Principal Investigator: C. Elbaum (Physics and Applied Mathematics).

Personnel: H. Kwun (Materials Research Laboratory).

Publication: "Finite Wave Amplitude Propagation in Solid and Liquid Helium 4," A. Hikata, H. Kwun, and C. Elbaum, Phys. Rev. *B21* (1980), 3932.

Supported by the Materials Research Laboratory/NSF.

Nonlinear Wave Interaction in a Dispersionless Liquid

In addition, nonlinear interactions of two ultrasonic waves, propagating collinearly in a dispersionless liquid medium were investigated.

Principal Investigator: C. Elbaum (Physics and Applied Mathematics).

Personnel: H. Kwun (Materials Research Laboratory).

Publication: "Nonlinear Interactions of Two Ultrasonics in a Dispersionless Liquid Medium," H. Kwun, A. Hikata, and C. Elbaum, J. Appl. Phys. *51* (1980), 4645.

Supported by the Materials Research Laboratory/NSF.

Anharmonic Properties of Liquid and Solid Helium

This study was undertaken in order to determine such features as higher (third) order elastic constants, wave coupling, and the response of dislocations (in solids) to high amplitude ultrasonic waves. To this end the amplitude response (i.e., relation between input and output amplitudes of a wave transmitted through a medium) of 10 MHz longitudinal wave is investigated in hcp and bcc solid ^{4}He as well as normal fluid and superfluid ^{4}He. In all four phases the acoustic saturation in the amplitude response curve was observed. The results are well described by an equation for amplitude loss based on second-harmonic generation. The nonlinear parameter β of these phases was evaluated. It is found that the magnitude β in solid ^{4}He is comparable to that of classical solids. Dislocation contributions to the amplitude response were also investigated and were ruled out as a significant source of the observed effects. It is concluded, therefore, that the large nonlinear amplitude response, which leads to saturation observed in solid ^{4}He should be attributed to the unusually large compressibility, i.e., small elastic constants (second order), which, in turn, induces in solid ^{4}He much larger strain amplitudes for a given applied stress than in ordinary solids.

Principal Investigator: C. Elbaum (Physics and Applied Mathematics).

Personnel: A. Hikata (Applied Mathematics) and H. Kwun (Materials Research Laboratory).

Publication: "Finite Amplitude Wave Propagation in Solid and Liquid ^{4}He," A. Hikata, H. Kwun, and C. Elbaum, Phys. Rev. *B1* (1980), 3932.

Supported by the Materials Research Laboratory/NSF.

Anharmonic Effects in Ultrasonic Propagation Near Second-Order Phase Transitions

Ultrasonic studies near second-order phase transitions have been extended here to sufficiently high amplitudes of the waves, so that nonlinear (anharmonic) behavior can be observed. In particular, anharmonic effects were studied by measuring the temperature dependence of second harmonics of a 10_4MHz ultrasonic wave generated near the λ transition of pressurized liquid ^{4}He. The anharmonic coupling coefficient C between the fundamental wave and the second harmonic is found to diverge as $\sim |t|^{-1}[t = (T/T_\lambda)-1]$ near T_λ. A phenomenological relation was developed expressing C in terms of known relevant thermodynamic quantities. This relation accounts well for the experimental results.

Principal Investigator: C. Elbaum (Physics and Applied Mathematics).

Personnel: A. Hikata (Applied Mathematics) and H. Kwun (Materials Research Laboratory).

SECTION 7

Other Research

Polymers

Recent experiments by Liao and Morawetz[1] show, contrary to physical intuition, that the activation energy for rotational barrier crossings in a long-chain molecule in solution is the same as for an analog molecule with only a single rotational barrier. We have studied this process by computer simulation, using the technique of Brownian dynamics applied to a model of a polymer chain regarded as a system of linked rigid bodies. The computer simulation results were found to agree qualitatively with the experimental results and provided insight into the reasons underlying the activation energy insensitivity.

---

[1]T.-P. Liao and H. Morawetz, Macromolecules *13* (1980), 1228.

Principal Investigator: J. H. Weiner (Engineering).

Personnel: D. Perchak (Physics).

Publication: "Activation Energy Insensitivity to Barrier-Crossing Correlations in Long-Chain Molecules," D. Perchak and J. H. Weiner, submitted to Macromolecules.

Supported by Materials Research Laboratory/GRI.

Dynamic Mechanical Response of Fiber-Reinforced Materials

A new program has been started to study the dynamic mechanical response of fiber-reinforced materials. Their response both when the deformations are elastic and plastic is being investigated, and at the same time, their fracture strength and the nature of crack propagation in such materials is being observed. This program is both experimental and theoretical and is being carried out in collaboration with Professor A. C. Pipkin.

The specimens used in these studies are of two types. First, specimens of Scotchply 2001 (an epoxy-resin reinforced with glass fibers) are being tested. Two types of Scotchply sheet have been obtained. In one the glass fibers are all oriented parallel to each other, in a single direction; in the other they are in the form of a square mesh, one half being in one direction and the other half in a direction perpendicular to it.

The other type of specimen which is being studied are beams of lead and tin, which have been reinforced along the beam direction either by steel piano wires or by wires of phospher-bronze. Three types of experimental test have been performed. These are (a) small elastic deformation, (b) large plastic deformation, and (c) crack propagation studies.

The Scotchply epoxy resin has been used in studies (a) and (c) and the metal specimens in studies (a) and (b). The experimental set-ups for the three types of investigation have been as follows: for (a) beams have been set into longitudinal, flexural and torsional resonance and from the resonant frequencies, the elastic moduli and the mode of deformation has been inferred; for (b) small charges of high explosive and high speed impacts in the "High G" testing machine have been carried out; while for (c) precracks have been inserted in the specimens which have been subjected to impact loads.

Interesting results have been obtained in all these investigations although they are all in the early stages of study. In particular it has been shown that when beam specimens with their fibers oriented parallel to the axis of the beam are set into flexural oscillation and the anisotropy of the material is very high (i.e., the ratio E/G is very large; E is the effective longitudinal modulus of the fibers and G is the shear modulus of the matrix) the dynamic

mechanical response of the material corresponds to G, the shear modulus of the material, rather than E, the extensional modulus of the fibers. (This is in agreement with the prediction of M. Sayir who very recently published a paper on this effect. Ing. Archiv. 49 (1980), 309-30.)

High speed cine-photographs of transverse dynamic impacts on fiber reinforced beams are being used to test the accuracy of the theoretical predictions of A. J. M. Spencer and his group on the response of such materials. Finally, measurements have been started on the dynamic stress intensity factors which occur when brittle fractures are propagated through sheets of fiber reinforced materials.

Work has also continued in a program, started earlier, on the anomalous torsional response of tubes of rubber subjected to large extensional strains. By studying the change in anomalous response of the behavior of specimens of a number of different rubbers at different temperatures, information has been obtained on the relation of the crystallization of the rubber to its biaxial mechanical response.

Principal Investigator: H. Kolsky (Applied Mathematics).

Personnel: S. Guofang (Applied Mathematics), J. Mosquera (Engineering), and P. Russo (Applied Mathematics).

Publications: "The Role of Stress Waves in Penetration Processes," H. Kolsky, chapter in *Ballistic Materials and Penetration Mechanics*, ed. by R. Laible (Elsevier Scientific Publishing Co., 1980), pp. 185-223.

"The Viscoelastic Response of Highly Stretched Rubber Specimens to Superposed Torsional Deformation," H. Kolsky and A. C. Pipkin, Ing. Archiv. 49 (1980), 337-45.

"The Anomalous Mechanical Response of Highly Stretched Tubes of Natural Rubber under Conditions of Biaxial Loading," J. Y. Liu, ARPA Technical Report AM 49 (1979).

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

Photoelectrolysis

Preparation and Comparison of the Photoelectronic Properties of $Sr_2Nb_2O_7$ and $Ba_{0.5}Sr_{0.5}Nb_2O_6$

The two alkaline earth niobates $Sr_2Nb_2O_7$ and $Ba_{0.5}Sr_{0.5}Nb_2O_6$ have been prepared, their electronic properties measured, and their photoresponses compared. The indirect band gap in $Sr_2Nb_2O_7$ is 3.86 eV compared with 3.38 eV for $Ba_{0.5}Sr_{0.5}Nb_2O_6$. Hence, photoanodes composed of $Sr_2Nb_2O_7$ respond to much less of the "white" light spectrum than those made from $Ba_{0.5}Sr_{0.5}Nb_2O_6$. Nevertheless, their electrical outputs at an anode potential of 0.8 eV with respect to SCE in 0.2 M soldium acetate under "white" xenon arc irradiation of 1.25 W/cm^2 are comparable.

Preparation and Photoelectronic Properties of $FeNbO_4$

The orthorhombic α-PbO_2 phase of $FeNbO_4$ was prepared and its photoelectronic properties measured: Sintered disks were shown to be n type and gave a resistivity of 40 Ω-cm. Measurements of the photoresponse gave a flat-band potential between 0.1 and 0.4 V vs SCE at a pH of 8.5 and an optical band gap of 2.08(2) eV. Several high-energy band gaps at 2.68(2), 3.24(2) and 4.38(2) eV were also determined. There appears to be an enhancement of the quantum efficiency due to the presence of $[FeO_6]$ active centers while retaining the fundamental characteristics of the $[NbO_6]$ octahedra.

Preparation and Photoelectronic Properties of the System $Cd_2Ge_{1-x}Si_xO_4$

Members of the system $Cd_2Ge_{1-x}Si_xO_4$ where $0 \le x \le 0.4$ have been prepared. These compounds were observed to crystallize with the olivine structure, space group Pbnm. The resistivity, Hall mobility, flat-band potential, band gaps, and stability were determined as functions of composition. The variation of these photoelectronic properties can be attributed to the reduction of the cell parameters with increasing silicon substitution. Substitution of silicon for Germanium reduces the loss of photocurrent from 25% after one hour for $\chi = 0.0$ to only 6% after

twenty-two hours for $\chi = 0.4$.

Principal Investigator: A. Wold (Chemistry).

Personnel: See below (Hydrodesulfurization Catalysts).

Publications: See below (Hydrodesulfurization Catalysts).

Hydrodesulfurization Catalysts

The Preparation and Properties of Poorly Crystallized CoS$_2$ and RuS$_2$

Amorphous or poorly crystallized samples of RuS$_2$ and CoS$_2$ were made by sulfurizing $(NH_4)RuCl_6$ and $(NH_3)CoCl_2$ at low temperatures with H$_2$S. The amorphous products were annealed under various conditions and the resulting degree of crystallinity was determined. For RuS$_2$, the average crystallite sizes ranged from 26Å for the poorly crystallized material, to greater than 2000Å for the well-crystallized material. CoS$_2$ average crystallite sizes ranged from 130Å to greater than 2000Å. The stoichiometry, appearance of the crystalline pyrite phases, cell parameters, and magnetic properties were studied as a function of annealing temperature.

Principal Investigator: A. Wold (Chemistry).

Personnel: A. Wold (Chemistry), K. Dwight (Chemistry), W. J. Croft (Chemistry), J. Hormadaly (Chemistry), S. N. Subbarao (Chemistry), R. Kershaw (Chemistry), B. Khazai (Chemistry), J. D. Passaretti (Chemistry), J. Koenitzer (Chemistry), R. R. Chianelli (Exxon Research & Development), and V. S. Nguyen (Chemistry).

Publications: "High Pressure Phase Transformation of Platinum Sulfide," A. Wold, R. Collins, R. Kaner, P. Russo, and D. Avignant, *Inorg. Chem. 18* (1979), 727.

"The Electrical, Optical and Photoconducting Properties of $Fe_{2-x}Cr_xO_3$ (0 x 0.47)," A. Wold, P. Merchant, R. Collins, R. Kershaw, and K. Dwight, *J. Solid State Chem. 27* (1979), 307.

"Interband Transitions of Semiconducting Oxides Determined from Photoelectrolysis Spectra," A. Wold, F. P. Koffyberg, and K. Dwight, *Solid State Comm. 30* (1979), 433.

"The Preparation of Amorphous RuS$_2$ at Ambient Temperature," A. Wold, J. D. Passaretti, and R. C. Collins, *Materials Res. Bull. 14* (1979), 1167.

"Preparation and Photoelectric Properties of n-Type Cd_2GeO_4," A. Wold, V. S. Nguyen, S. N. Subbarao, R. Kershaw, and K. Dwight, *Materials Res. Bull. 14* (1979), 1535.

"Electrical and Optical Properties of High-Purity p-Type Single Crystals of $GeFe_2O_4$," A. Wold, P. Strobel, and F. P. Koffyberg, *J. Solid State Chem. 31* (1980), 209.

"Preparation and Properties of a Copper Niobium Oxyfluoride," A. Wold, B. Khazai, K. Dwight, and E. Kostiner, *Inorg. Chem. 19* (1980), 1670.

"Preparation and Comparison of the Photoelectric Properties of $Sr_2Nb_2O_7$ and $Ba_{0.5}Sr_{0.5}Nb_2O_6$," A. Wold, J. Hormadaly, S. N. Subbarao, R. Kershaw, and K. Dwight, *J. Solid State Chem. 33* (1980), 27.

Investigations of Solar Cells Based on Chalcopyrite Semiconductors and Their Alloys

In the previous MRL Annual Technical Report, we summarized the reasons for the interest in the chalcopyrite semiconductors, of which $CuInSe_2$ is a prototype, for solar cell applications. Briefly, it has already been shown that photovoltaic devices that can convert somewhat more than 10% of the sunlight incident on them into electricity can be fabricated from single crystals of $CuInSe_2$ and that cells having efficiencies up to 6% can be fabricated from thin films of $CuInSe_2$. Our group at Brown has focused its attention on alloys of these ternary chalcopyrites like $CuIn_yGa_{1-y}Se_{2z}Te_{2(1-z)}$ in which one can prepare semiconductors having a wide range of bandgaps. Such materials can be combined with a wide bandgap semiconductor like CdS to produce heterojunction photovoltaic cells in which there is no lattice mismatch and in which intrinsic interface state concentrations should have a negligible concentration. Solar cells made from such pairs of lattice matched semiconductors should attain higher efficiencies than cells like the n-CdS/p-$CuInSe_2$ cells in which lattice mismatch is about 1%.

During the period 1 July 1979 through 30 June 1980, we have continued our work on these materials and on solar cells fabricated from them. We have continued to synthesize powders of four and five element alloys of $Cu_xAg_{(1-x)}InS_{2z}Se_{2(1-z)}$ and of $CuIn_yGa_{(1-y)}Se_{2z}Te_{2(1-z)}$. Targets for rf-sputtering were prepared from these synthesized powders. Thin films of the Cu-In-Ga-Se-Te system were deposited by sputtering from these targets. The alloys chosen for sputtering had forbidden energy bandgaps of about 1.25 eV, 1.35 eV and 1.45 eV, all with the same lattice constant as CdS. Optical transmission measurements on these films indicated that the bandgaps were close to their anticipated values. X-ray diffraction studies showed that they had either the sphalerite or the chalcopyrite structure. Analysis of EDAX spectra indicated that the films were essentially stoichiometric. SEM studies showed that grain sizes of 1 um were achievable; such grain sizes are compatible with acceptable efficiency photovoltaic cells. Devices made from such films by covering them with evaporated films of CdS had open circuit voltages of 0.5 V but their other photovoltaic properties were poor so that their overall solar energy conversion efficiency was low. Identification of the factors limiting the photovoltaic characteristics of these films is the target of continuing research in this area.

Films of the ternaries and ternary alloys were also deposited by chemial spray pyrolysis, a deposition technique which is even more attractive from an economic point of view than rf-sputtering. Briefly, to deposit films by this method an aqueous solution containing a stoichiometric proportion of the ions in the desired material is sprayed as a fine mist over a glass substrate which is heated to a temperature between 200°C and 400°C. When the mist strikes the substrate, the desired ions deposit on the glass and form the compound and the other products of the reaction volatilize. We have prepared thin films of $CuInS_2$, $CuInSe_2$, $AgInS_2$, and of four and five element alloys of the Cu-Ag-In-S-Se system by this method. Photovoltaic cells have been made from these films by evaporating CdS over them.

We have also continued working on Semiconductor-Insulator-Semiconductor (SIS) solar cells. Large area (4 cm^2) devices, having solar energy conversion efficiencies up to 14%, have been made by depositing a thin layer of indium-tin-oxide (ITO) over single crystal silicon. The ITO was deposited by argon-beam sputtering. The performance of these SIS devices is comparable to that of single crystal solar cells in which the p/n junction is formed by diffusion.

We have also completed theoretical calculations on the ultimate efficiency which can be expected from new design solar cells which employ minority carrier mirrors and optical mirrors. A minority-carrier-mirror (MCM) is an electrostatic barrier, internal to the photovoltaic cell, at which minority carriers are reflected back toward the charge-separating p/n junction. Such MCM's can increase the open circuit voltage of PV cells if the separation between the p/n junction and the MCM is less than the minority carrier diffusion length. Our calculations show that the efficiency of thin film direct gap photovoltaic cells, specifically $CuInSe_2$ cells, can in principle attain a value of 26% in cells whose total thickness lies between one and two microns. The insight provided by these calculations is guiding our experiments; we are trying to realize the benefits of MCM's in ternary semiconductor solar cells fabricated by rf-sputtering.

Finally, we have been exploring application of these theoretical concepts to germanium cells intended for thermo-photovoltaic energy converters (TPV) which are of interest to the Naval Research Laboratories. As the experimental part of this effort we have measured the minority carrier recombination velocity at the interface between germanium crystals and a native oxide, produced by high pressure oxidation, by the transient capacitance method.

REFERENCES

"Ion Implanted Grating Type Silicon Solar Cells," R. S. Tang, H. L. Hwang, and J. J. Loferski, Proc. 14th IEEE Photovoltaic Specialists Conf., January 1980.

"The Application of Pentenary Alloy Compounds of the $Cu_{1-y}Ag_yInS_{2(1-x)}$, $A^I_{1-y}B^I_yC^{III}E^{IV}_{2(1-x)}$ Variety to Photovoltaic Solar Energy Conversion," J. Shewchun, J. J. Loferski, D. Burk, B. K. Garside, R. Beaulieu, and D. Polk, Proc. 14th IEEE Photovoltaic Specialists Conf., January 1980.

"Rf-Sputtered $CuInSe_2$ Thin Films," J. Piekoszewski, J. J. Loferski, R. Beaulieu, J. Beall, B. Roessler, and J. Shewchun, Solar Energy Materials 2 (1980), 363-72.

"Spray Pyrolysis of $CuInSe_2$ Thin Films," M. Gorska, R. Beaulieu, J. J. Loferski, B. Roessler, and J. Beall, Solar Energy Materials 2 (1980), 343-45.

"Spray Pyrolysis of Silver-Indium Sulfides," M. Gorska, R. Beaulieu, J. J. Loferski, and B. Roessler, Thin Solid Films 67 (1980), 341.

"Single Crystal Solar Cell Heterojunctions Involving n-Cadmium Sulfide," M. Arienzo and J. J. Loferski, J. Appl. Phys., July 1980.

Publications: "$Cu_{1-y}Ag_yInS_{2(1-x)}$, Prototype of the Pentenary Chalcopyrite Semiconductor System for Photovoltaic Cells," G. H. Chapman, J. J. Loferski, J. Shewchun, R. Beaulieu, and B. K. Garside, Solar Energy Materials (August 1979), 451-70.

"Lattice Constants and Bandgap Variations of the Pentenary Semiconductor System $Cu_{1-y}Ag_yInS_{2(1-x)}$," G. H. Chapman, J. Shewchun, J. J. Loferski, B. K. Garside, and R. Beaulieu, Solar Energy Materials (August 1979).

"Thin Films and Solar Energy Application," J. J. Loferski, Surface Sci. 86 (1979), 424.

"Semiconductor-Insulator-Semiconductor (SIS) Solar Cells: Indium-Tin-Oxide on Silicon," J. J. Loferski, M. Spitzer, D. Burk, J. Shewchun, J. Kukula, R. Singh, and F. Sholz, Proc. 14th IEEE Photovoltaic Specialists Conf., January 1980.

"Theoretical Limit Efficiency of Direct Gap Homojunction Solar Cells," M. Spitzer, J. J. Loferski, and J. Shewchun, Proc. 14th IEEE Photovoltaic Specialists Conf., January 1980.

"Ultra High Efficiency Thin Silicon p-n Junction Solar Cells Using Reflecting Surfaces," J. Shewchun, J. J. Loferski, M. Spitzer, and J. Kukula, Proc. 14th IEEE Photovoltaic Specialists Conf., January 1980.

"Thin Film p-$CuInSe_2$/n-CdS Solar Cells in Which the $CuInSe_2$ Is Prepared by Rf-Sputtering," with J. Piekoszewski, J. Beall, J. J. Loferski, B. Roessler, J. Shewchun, and R. Beaulieu, Proc. 14th IEEE Photovoltaic Specialists Conf., January 1980.

Nonequilibrium Plasmas in Semiconductors

Recently developed picosecond infrared techniques have been applied to the study, for the first time, of the real time dynamics of dense, highly degenerate, transient electron hole systems in PbTe, InSb, and $Hg_{1-x}Cd_xTe$. In these experiments an intense ultrashort pulse generated a high density electron-hole gas ($\cdot 10^{19}cm^{-3}$) through interband absorption $\hbar\omega \gg E_g$. The optical properties of the excited system were then examined by picosecond infrared radiation at 10.6 μm and 5.3 μm wavelengths corresponding to probing of intraband and near band edge interband transitions, respectively. From time resolved decay measurements we have determined concentration

dependent recombination rates, dominated most likely by rapid Auger processes. For example, a characteristic decay time of ≤ 40 psec was measured in PbTe at room temperature at an excess density of ~10^{19}cm^{-3}. Measurements for InSb and Hg$_x$Cd$_x$Te have also yielded data for picosecond relaxation rates at the high excess densities and at varying temperatures. In interpreting the results, initial attempts have been made to include in the dielectric modeling the contribution by many-body effects, which appear to be quite significant in our experimental conditions. In this we have been aided by experimental measurements of the "dynamic" plasma edge ($\omega = \omega_p(t)$) and time varying interband transition rates (absorption and gain) at the probe beam frequencies.

Elsewhere we have theoretically examined the guiding of millimeter waves as interface electromagnetic waves (surface plasmons) in moderately doped semiconductors of high material quality. Specifically, we have calculated the propagation characteristics and modulation of surface plasmons in n-GaAs. Our results suggest that useful guiding and control of millimeter wave signals by these excitations may be possible.

Principal Investigator: A. V. Nurmikko (Engineering).

Personnel: W. Lemley (Engineering) and J. Ajo (Engineering).

Publications: "Study of Surface Recombination in GaAs and InP by Picosecond Optical Techniques," A. V. Nurmikko, C. A. Hoffman, and H. J. Gerritsen, J. Appl. Phys. *51* (1980), 1603.

"Generation of Ultrashort Pulses in Synchronous Pumping of Near-Millimeter Wave Lasers," A. V. Nurmikko and W. Lemley, J. Infrared and MM-waves *1* (1980), 85.

"Guiding and Control of Millimeter Waves by Surface Plasmon Phenomena in Semi-conductors," A. V. Nurmikko, D. M. Bolle, and S. Talisa, J. Infrared and MM-waves *1* (1980), 3.

"Nonlinear Transmission of Picosecond 10.6 um Pulses in InSb," B. D. Schwartz and A. V. Nurmikko, Optics Letters *5* (1980), 5.

"Picosecond Infrared Spectroscopy in Narrow-Gap Semiconductors," B. D. Schwartz and A. V. Nurmikko, in Picosecond Phenomena II, Springer-Verlag Series in Chemical Physics *14* (1980), p. 303.

Theory of the Hall Effect in Amorphous Semiconductors

Charge transport in amorphous semiconductors is generally assumed to occur in two regimes: extended state motion for carriers with energies above the mobility edge, and transport among Anderson localized states for carriers with energies below the edge. In the former regime, the scattering is strong and the mean free path of the order of the interatomic spacing, too small for conventioanl Bloch-Wilson band theory to apply. The random phase model has been used here, where phase coherence of the one electron wave function is taken to be random from one site to the next. In one part of our study, it was shown that this model leads to difficulties which can be avoided by taking the phases to be correlated over the mean free path (phase correlation distance) but taking phase differences of distinct pairs of sites to be uncorrelated. In particular, it was shown that the previously derived expression for the Hall mobility uH is recovered—an expression which has been successfully applied to transport data in a number of disordered systems and liquid semiconductors.

In fitting the temperature dependence of a number of transport properties of amorphous semiconductors, many workers (notably N. F. Mott and his school) assume a two band model in which the partial Hall effect due to the localized states is negligible in comparison to that of the extended states described above. In order to investigate the validity of this assumption, we have studied the Hall effect due to hopping transport in systems with both random site position and random local site energies (earlier studies incorporated the former but neglected the latter). We have carried out a percolation-theoretic calculation of the Hall effect for this case and find that for statistical reasons the Hall mobility is indeed very small as had been assumed.

Principal Investigator: L. R. Friedman (Physics).

X-Ray Topography

Studies of oxidation in zinc by x-ray topography and correlation with surface features observed by scanning electron microscopy, microprobe and optical and Nomarski microscopy have continued. Electron microprobe measurements of the oxygen and zinc x-ray intensities, in regions of crystal surface selected on the basis of optical and x-ray topographic observations, indicate that a correlation exists between the surface defects, oxide growth and lattice defects. Berg Barrett x-ray topographs show the dislocation structure within the crystal and its alteration during oxide growth on the surface. Loop and spiral dislocations are observed in the presence of large numbers of slip dislocations of all three basal Burger's vectors. Dislocation spirals are often composed of bundles of these dislocations. Dislocation loop growth and climb of dislocation spirals, associated with vacancy injection into the lattice during oxidation, are observed during oxidation at room temperature. Hexagonal crystallographic pits are observed optically on the crystal surface which give a correlatable contrast in Berg Barrett topographs. The results indicate that the oxidation process is closely related to and perhaps controlled by the lattice defect density and dislocation arrangements near the surface.

In addition, a small effort has been devoted to activities based on work carried out in the past on x-ray topographic observations of ferromagnetic domains and associated contrast effects and on small angle grain boundaries in zinc crystals. These activities were in connection with the U.S.-France Seminar on Applications of x-ray topography to Materials Science held March 12-14, 1980 in Paris, France. As an outgrowth of these activities we have also begun preparations for some work using synchrotron radiation for topography in cooperation with Dr. Masao Kuriyama of the National Bureau of Standards in Washington, DC.

Principal Investigator: B. Roessler (Engineering).

Personnel: K. C. Yoo (Engineering) and W. Oates (Engineering).

Nonlinear Wave Interactions in Condensed Matter

The study of nonlinear (anharmonic) properties of solids and liquids has a long history. Many questions in this area, however, remain unanswered. One of these questions concerns parametric amplification under special conditions. We conducted, therefore, a study of this problem.

Nonlinear interactions of two ultrasonic waves, propagating collinearly in a dispersionless liquid medium, are investigated experimentally for both degenerate and nondegenerate cases. Results are described of the first experimental observation of parametric amplification of the signal wave for the degenerate case. For the nondegenerate case, no such amplification of the amplitude of the signal wave is observed. These experimental results are found to be in good agreement with the results of the theoretical analysis presented in the paper.

Principal Investigator: C. Elbaum (Physics and Applied Mathematics).

Personnel: A. Hikata (Applied Mathematics) and H. Kwun (Materials Research Laboratory).

Lecturers in the Materials Research Laboratory Program, 1979-80

September 20, 1979

Solid State Seminar: Physics Department, Dr. Erio Tosatti, International Center for Theoretical Physics and the University of Trieste, Italy, INSTABILITIES, PHASE TRANSITIONS AND MEETING OF CRYSTAL SURFACES.

September 24, 1979

Physics Colloquium: Professor F. M. Pipkin, Department of Physics, Harvard University, MEASUREMENTS OF THE FINE STRUCTURE OF HYDROGENIC ATOMS.

September 26, 1979

Materials Science Seminar: Division of Engineering, Professor John Hirth, Department of Metallurgical Engineering, Ohio State University, MICROSTRUCTURAL MODELS FOR FRICTION AND WEAR.

September 27, 1979

Joint Materials Science and Fracture Group Seminar: Division of Engineering, Dr. John Hancock of the Department of Mechanical Engineering, University of Glasgow, DUCTILE FRACTURE.

Solid State Seminar: Physics Department, Dr. T. N. Taylor, Los Alamos Scientific Lab, SURFACE STUDIES OF UO_2 BY LOW ENERGY ELECTRON DIFFRACTION AND ION SCATTERING SPECTROSCOPY.

October 3, 1979

Materials Science Seminar: Division of Engineering, Dr. A. F. Szewczyk, Brown University, MICROSTRUCTURAL OBSERVATIONS OF MONOTONICALLY AND CYCLICALLY DEFORMED DUAL-PHASE STEEL.

October 4, 1979

Theoretical Seminar: Physics Department, Dr. Goran Senjanovic, Department of Physics, University of Maryland, BROKEN SYMMETRIES AT HIGH TEMPERATURE.

October 11, 1979

Solid State Seminar: Physics Department, Professor Brooke Gregory, Trinity College, MAGNETIZATION OF MULTIPLY-CONNECTED SUPERCONDUCTORS.

October 15, 1979

Solid Mechanics Seminar: Division of Engineering, Professor K. B. Broberg, Lund Institute of Technology, CRACK PROPAGATION BEYOND THE RAYLEIGH WAVE VELOCITY.

October 18, 1979

Theoretical Seminar: Physics Department, Dr. Tom Clark, Los Alamos, AXIAL CURRENTS, SUPERCURRENTS AND ANOMALIES.

Solid State Seminar: Physics Department, Dr. Walter Bloss, Physics Department, Brown University, *EXCHANGE-CORRELATION INDUCED TRANSITION IN SILICON INVERSION LAYERS.*

October 22, 1979

Solid Mechanics Seminar: Division of Engineering, Dr. Viggo Tvergaard, Department of Solid Mechanics, Technical University of Denmark, INFLUENCE OF VOIDS ON SHEAR BAND INSTABILITIES UNDER PLANE STRAIN CONDITIONS.

October 23, 1979

Materials and Electrical Sciences Seminar: Division of Engineering, Professor Julian Aulytner, Central Laboratory of X-Ray and Electron Microscopy, Polish Academy of Sciences, Warsaw, Poland, X-RAY AND ELECTRON MICROSCOPIC INVESTIGATION OF ION-IMPLANTED CRYSTALS.

October 25, 1979

Solid State Seminar: Physics Department, Professor L. Friedman, St. Andrews University, Scotland, and Brown University, THE HALL EFFECT IN AMORPHOUS AND LIQUID SEMICONDUCTORS.

October 26, 1979

Chemistry Colloquium: Dr. F. Stillinger, Bell Laboratory, BRIDGING STRUCTURAL CHEMISTRY AND STATISTICAL MECHANICS WITH THE POLARIZATION MODEL.

November 1, 1979

Solid State Seminar: Physics Department, Dr. U. Strom, Naval Research Laboratory, DISORDER PHENOMENA IN SUPERIONIC CONDUCTORS.

Solid Mechanics Seminar: Division of Applied Mathematics, Dr. Paolo Podio-Guidugli, Department of Mathematics, Carnegie-Mellon University, SOME QUALITATIVE ASPECTS IN STRUCTURAL STABILITY.

November 5, 1979

Physics Colloquium: Dr. L. Nosanow, National Science Foundation, SPIN ALIGNED HYDROGEN; A POSSIBLE NEW QUANTUM SYSTEM.

November 7, 1979

Joint Applied Mathematics and Solid Mechanics Seminar: Divisions of Applied Mathematics and Engineering, Professor William Prager, Savognin, Switzerland, SOME UNEXPECTED RESULTS IN STRUCTURAL OPTIMIZATION.

November 15, 1979

Solid State Seminar: Physics Department, Professor E. Abrahams, Rutgers University, LOCALIZATION AND NON-OHMIC EFFECTS IN TWO DIMENSIONS.

November 16, 1979

Chemistry Colloquium: Dr. M. Saunders, Yale University, NON-CLASSICAL DELOCALIZATION IN CATIONS BY NMR.

November 19, 1979

Solid Mechanics Seminar: Division of Engineering, Dr. C. T. Chon, Ford Scientific Research Labs, ANALYSIS OF COMPOSITE DRIVE SHAFT AND TUBULAR LAP JOINT.

November 20, 1979

Solid State Seminar: Physics Department, Dr. James Smith, Los Alamos Scientific Lab, SUPERCONDUCTIVITY IN F-ELECTRON SYSTEMS.

Chemistry Colloquium: Dr. R. Silbey, Massachusetts Institute of Technology, ELECTRONIC ENERGY TRANSFER IN DISORDERED SOLIDS.

November 26, 1979

Physics Colloquium: Professor N. Ashcroft, Department of Physics, Cornell University, VERY DENSE PHASES OF HYDROGEN.

November 28, 1979

Materials Science Seminar: Division of Engineering, Dr. Alan T. English, Supervisor Reliability Studies, Bell Laboratories, Murray Hill, New Jersey, PHOTOLITHOGRAPHY UTILIZING INORGANIC RESISTOR MATERIALS.

November 29, 1979

Solid State Seminar: Physics Department, Dr. David Zehner, Oak Ridge National Laboratory, GEOMETRICS: SURFACE STRUCTURE VIA HIGH ENERGY ION SCATTERING.

December 3, 1979

Physics Colloquium: Professor Nihat Berker, Department of Physics, Massachusetts Institute of Technology, RENORMALIZATION GROUP THEORY: PHASE TRANSITIONS IN ABSORBED SYSTEMS.

December 5, 1979

Materials Science Seminar: Mr. Henry Cialone, Materials Science Division, Brown University, THE ROLE OF HYDROGEN IN THE DUCTILE FRACTURE OF PLAIN CARBON STEELS.

December 6, 1979

Solid State Seminar: Physics Department, Dr. Norton Lang, IBM, Yorktown Heights, CORE HOLES AND CHEMISORPTION.

December 7, 1979

Solid Mechanics Seminar: Division of Engineering, Professor Sol Bodner, Division of Mechanical Engineering, Technion, Haifa, Israel, DEVELOPMENT AND APPLICATION OF MULTI-DIMENSIONAL HARDENING LAWS FOR ELASTIC-VISCOPLASTIC MATERIALS.

December 10, 1979

Solid Mechanics Seminar: Division of Engineering, Dr. John Dempsey, Department of Civil Engineering, Northwestern University, SOME REMARKS ON SINGULAR SOLUTIONS IN PLANE ELASTICITY.

December 12, 1979

Solid Mechanics Seminar: Division of Engineering, Professor Eric Reissner, University of California at San Diego, NEW THOUGHTS ON THE PROBLEM OF BENDING AND TWISTING OF BEAMS.

December 13, 1979

Solid State Seminar: Physics Department, Dr. H. K. Henish, Department of Physics, Pennsylvania State University, RELAXATION SEMICONDUCTORS.

December 14, 1979

Physics Colloquium: Professor T. W. Ruijgrok, Institute voor Theoretische Fysica, The Netherlands, ON THE HAMILTONIAN AND LAGRANGIAN FORMULATION OF CLASSICAL DYNAMICS FOR PARTICLES WITH SPIN.

January 7, 1980

Solid Mechanics Seminar: Division of Engineering, Professor Michael P. Cleary, Department of Mechanical Engineering, Massachusetts Institute of Technology, SOME MECHANICS ASPECTS OF UNDERGROUND FRACTURING.

January 9, 1980

Materials Science Seminar: Division of Engineering, Dr. M. P. Puls, Whiteshell Nuclear Research Establishment, Atomic Energy of Canada Ltd., Pinawa, Manitoba, STRAIN ENERGY EFFECTS AND HYDRIDE INDUCED CRACK GROWTH.

January 11, 1980

Chemistry Colloquium: K. Eisenthal, Columbia University, PICOSECOND LASER STUDIES OF PROTON TRANSFER PROCESSES.

Solid Mechanics Seminar: Division of Engineering, Professor Atle Gjelsvik, Department of Civil Engineering, Columbia University, PLASTIC ANALYSIS IN OFFSHORE STRUCTURES.

February 1, 1980

Chemistry Colloquium: Dr. T. Madey, National Bureau of Standards, USE OF ELECTRON STIMULATED DESORPTION FOR DETERMINING THE STRUCTURES OF ABSORBED MOLECULES.

February 7, 1980

Solid State Seminar: Physics Department, Dr. David Emin, Sandia Laboratory, Albuquerque, New Mexico, POLARON VERSUS DEFECT PICTURE IN AMORPHOUS SEMICONDUCTORS.

February 8, 1980

Chemistry Colloquium: Dr. Gary Pruentt, University of Pennsylvania, STATE SELECTED REACTIONS UNDER MOLECULAR BEAM CONDITIONS.

February 14, 1980

Division of Applied Mathematics Seminar: Dr. Jerry Nedelman, Cornell University Graduate School of Medical Sciences, Biomathematics Division, FACILITATED DIFFUSION OF OXYGEN AND CARBON MONOXIDE IN THE HIGH AFFINITY REGIME.

Energy Lecture: Physics Department, Professor E. A. Farber, University of Florida, Gainesville, Florida, SOLAR ENERGY: ITS CONSERVATION AND UTILIZATION.

February 15, 1980

Solid State Seminar: Physics Department, Dr. Jorge Hirsch, University of Chicago and University of California, San Diego, SINGULAR THERMODYNAMIC PROPERTIES OF RANDOM MAGNETIC CHAINS.

February 20, 1980

Materials Science Seminar: Division of Engineering, John Fisher, Brown University, VOID NUCLEATION IN SPHEROIDIZED STEELS DURING TENSILE DEFORMATION.

February 21, 1980

Solid State Seminar: Physics Department, Dr. James W. Davenport, Brookhaven National Laboratory, Long Island, CHEMISORPTION AND SOLUTION OF HYDROGEN IN TRANSITION METALS.

February 22, 1980

Chemistry Colloquium: Dr. Mark M. Green, New York Polytechnical Institute, MASS SPECTROMETRY IS NOT SPECTROMETRY.

February 29, 1980

Solid State Seminar: Physics Department, Professor E. Burstein, University of Pennsylvania, GIANT RAMAN SCATTERING BY MOLECULES ON METAL SURFACES.

March 6, 1980

Solid State Seminar: Physics Department, Dr. D. R. Hamann, Bell Telephone Laboratories, CHEMISORPTIVE BONDS ON SEMICONDUCTORS: STRUCTURE AND SPECTRA.

March 7, 1980

Chemistry Colloquium: Dr. J. R. Dorfman, University of Maryland, ELEMENTARY EXCITATIONS IN CLASSICAL LIQUIDS.

Division of Applied Mathematics Colloquium: Professor N. J. Zabusky, University of Pittsburgh, VORTEX DYNAMICS: STABILITY, INTERACTIONS AND BREAKING OF COHERENT STRUCTURES.

March 10, 1980

Physics Colloquium: Professor James S. Langer, Department of Physics, Carnegie-Mellon University, INSTABILITIES AND PATTERN FORMATION IN SOLIDIFICATION.

March 12, 1980

Solid Mechanics Seminar: Division of Engineering, Professor Alan Needleman, Brown University, FLOW-LOCALIZATION IN THE PLANE TENSILE TEST.

March 13, 1980

Solid State Seminar: Physics Department, Professor Leo P. Kadanoff, University of Chicago, THE WORK OF SATO, MIWA AND JIMBO: THE ISING MODEL AND THE DIRAC EQUATION.

March 14, 1980

Division of Applied Mathematics Seminar: Dr. Nicholas Alikakos, Purdue University, ON THE EQUATION OF POROUS MEDIA.

March 17, 1980

Physics Colloquium: Dr. Arthur Ashkin, Bell Telephone Laboratories, TRAPPING OF PARTICLES BY LASER LIGHT.

March 20, 1980

Solid Mechanics Seminar: Division of Engineering, Dr. R. D. James, Department of Aeronautical Engineering and Mechanics, University of Minnesota, CO-EXISTENT PHASES IN ELASTICITY.

Solid State Seminar: Physics Department, Professor Samuel C. Fain, Jr., University of Washington, Seattle, PHASE TRANSITIONS IN PHYSISORBID LAYERS.

March 24, 1980

Solid Mechanics Seminar: Division of Engineering, Professor A. J. Holzer, Department of Mechanical Engineering, Carnegie-Mellon University, DYNAMIC MECHANICAL PROPERTIES USING SHORT LOAD CELLS.

March 27, 1980

Energy Lecture: Department of Physics, Dr. Richard T. Kennedy, Commissioner, United States Nuclear Regulatory Commission, AVAILABILITY OF PRIMARY ENERGY RESOURCES AND TECHNOLOGY.

April 11, 1980

Chemistry Colloquium: Dr. Hans Nowotny, University of Connecticut, STRUCTURAL PRINCIPLES OF ALLOY PHASES.

April 14, 1980

Expository Talk: Division of Applied Mathematics, Mr. Paul Massatt, Brown University, STABILITY AND FIXED POINTS OF DISSIPATIVE SYSTEMS.

April 17, 1980

Solid State Seminar: Department of Physics, Dr. Douglas Osheroff, Bell Telephone Laboratories, NUCLEAR ANTIFERROMAGNETIC RESONANCE AND SOLID He^3.

April 21, 1980

Solid Mechanics Seminar: Division of Engineering, Dr. Shiro Kubo, Osaka University, Japan, A PHENOMENOLOGICAL ANALYSIS OF CREEP CRACK PROPAGATION IN DUCTILE MATERIALS.

Physics Colloquium: Professor Paul Meijer, Catholic University of America, Washington, DC, SUPERCOOLING OF WATER AND OTHER LIQUIDS.

Materials Science Seminar: Division of Engineering, Dr. -Ing J. Heinrich, Deutsche Forschungs-und Versuchsanstalt fur Luft-und Raumfahrt, E.V., PROCESSING OF STRUCTURAL CERAMICS.

April 28, 1980

Solid Mechanics Seminar: Dr. J. W. Nunziato, Sandia Laboratories, A THEORY OF MULTI-PHASE MIXTURES WITH APPLICATIONS TO TWO-PHASE FLOWS.

May 1, 1980

Solid State Seminar: Department of Physics, Dr. D. Greywall, Bell Telephone Laboratories, THE He^3 QUASIPARTICLE SPECTRUM FOR DILUTE SOLUTIONS OF He^3 IN SUPERFLUID He^4.

May 7, 1980

Materials Science Seminar: Professor R. O. Heckroodt, Department of Materials Science, University of Capetown, South Africa, TELLURITE GLASSES AND RARE EARTH PHOTOCHROMISM.

May 8, 1980

Solid State Seminar: Department of Physics, Dr. R. Penn, National Bureau of Standards, EFFECT OF d-BAND HOLES ON THE PHOTOEMISSION SPECTRUM OF Ni.

Solid Mechanics Seminar: Division of Engineering, Professor William N. Findley, Brown University, THE COMBINED TENSION AND TORSION CREEP AND RELAXATION OF 2618 A AT 200 C UNDER VARIABLE NONLINEAR STRESSES.

May 9, 1980

Materials Science Seminar: Division of Engineering, Professor I. M. Bernstein, Department of Metallurgy and Materials Science, Carnegie-Mellon University, MICROMECHANICS OF CLEAVAGE FRACTURE IN EUTECTOID STEELS.

May 12, 1980

Solid Mechanics Seminar: Division of Engineering, Professor Janusz Klepaczko, Institute of Fundamental & Technological Research, Warsaw, Poland and the Division of Engineering, Brown University, LOADING RATE SPECTRA IN FRACTURE DYNAMICS.

May 13, 1980

Seminar on Identification and Control: Division of Applied Mathematics, Professor B. Jakubczyk, Polish Academy of Science, Warsaw, Poland and the Division of Applied Mathematics, Brown University, REALIZATIONS OF NONLINEAR SYSTEMS.

May 19, 1980

Solid Mechanics Seminar: Division of Engineering, Professor William A. Nash, Department of Civil Engineering, University of Massachusetts, SEISMIC EFFECTS ON LIQUID STORAGE TANKS.

June 20, 1980

Materials Science Seminar: Division of Engineering, Dr. Jean Louis Chermant, Laboratory of Crystallography and Chemistry of Solids, University of Caen, Caen, France, SINTERING: THEORY AND TOPOLOGY.

List of Staff in the Materials Research Laboratory Program

APPLIED MATHEMATICS

NAME	*TITLE*
C. Elbaum	Professor (Physics)
H. Kolsky	Professor (Engineering) (Physics)
A. C. Pipkin	Professor
A. Hikata	Professor (Research)
L. Mannion	Research Assistant
J. Mosquera	Research Assistant
J. Marsella	Technical Assistant
P. Russo	Technical Assistant

List of Staff in the Materials Research Laboratory Program

CHEMISTRY

NAME	TITLE
R. H. Cole	Professor
P. J. Estrup	Professor (Physics)
E. F. Greene	Professor
W. M. Risen, Jr.	Professor
A. Wold	Professor (Engineering)
K. Dwight	Associate Professor
G. J. Diebold	Assistant Professor
J. Hormadly	Research Associate
S. N. Subbarao	Research Associate
R. A. Barker	Research Assistant
D. M. Barnes	Research Assistant
J. Hayden	Research Assistant
E. I. Kamitsos	Research Assistant
J. Keeley	Research Assistant
B. Khazai	Research Assistant
V. S. Nguyen	Research Assistant
J. D. Passaretti	Research Assistant
M. Pickering	Research Assistant
C. H. Tzinis	Research Assistant
C. H. Windisch	Research Assistant
J. Koenitzer	Research Undergraduate Student

List of Staff in the Materials Research Laboratory Program

ENGINEERING

NAME	TITLE
R. J. Asaro	Professor
D. H. Avery	Professor
R. J. Clifton	Professor
J. Duffy	Professor
L. B. Freund	Professor
M. Glicksman	Professor
J. Gurland	Professor
G. S. Heller	Professor
H. Kolsky	Professor
	(Applied Mathematics)
	(Physics)
J. J. Loferski	Professor
J. R. Rice	Professor
M. H. Richman	Professor
B. Roessler	Professor
J. Tauc	Professor
	(Physics)
J. H. Weiner	Professor
	(Physics)
A. Wold	Professor
	(Chemistry)
A. Needleman	Associate Professor
A. V. Nurmikko	Associate Professor
K. K. Lo	Assistant Professor
J. Klepaczko	Visiting Professor, Research
J. Shewchun	Visiting Professor
V. Tvergaard	Visiting Associate Professor
P. Kumar	Visiting Assistant Professor
X. Markenscoff	Visiting Assistant Professor
J. Piekoszewski	Senior Research Associate
S. Kubo	Postdoctoral Research Fellow
L. Bieman	Research Associate
R. Dmowska	Research Associate, Geological Sciences
Z. Vardeny	Research Associate
I. Abou-Sayed	Research Assistant
J. Ajo	Research Assistant
J. M. Baik	Research Assistant
P. Burgers	Research Assistant
D. Burk	Research Assistant
C. Case	Research Assistant
H. Cialone	Research Assistant

R. Deshmukh	Research Assistant
A. Douglas	Research Assistant
W. J. Drugan	Research Assistant
Y. Ercil	Research Assistant
J. R. Fisher	Research Assistant
A. Gilat	Research Assistant
O. Gregory	Research Assistant
J. Hong	Research Assistant
M. Kachanov	Research Assistant
F. K. Lehner	Research Assistant
W. Lemley	Research Assistant
C. H. Li	Research Assistant
V. C. Li	Research Assistant
M. Magida	Research Assistant
A. Morrone	Research Assistant
J. Mosquera	Research Assistant
J. Pan	Research Assistant
D. Perchak	Research Assistant
D. Pierce	Research Assistant
A. Rosakis	Research Assistant
A. Rubenstein	Research Assistant
A. Ruina	Research Assistant
T. L. Sham	Research Assistant
A. Szewczyk	Research Assistant
N. Triantafyllidis	Research Assistant
K. C. Yoo	Research Assistant
R. Zeller	Research Assistant
J. C. Lambropolis	Undergraduate Student
T. Simon	Undergraduate Student
E. E. Crisman	Senior Research Engineer
R. H. Hawley	Senior Research Engineer
L. Hermann	Senior Research Engineer
B. Agbara	Research Engineer
J. Beall	Research Engineer
R. Kershaw	Research Engineer
T. Kirst	Research Engineer
R. Beaulieu	Technical Assistant
J. W. Fogarty	Technical Assistant
G. J. LaBonte	Technical Assistant
W. Oates	Technical Assistant
P. Rush	Technical Assistant
H. Stanton	Technical Assistant

List of Staff in the Materials Research Laboratory Program

MATERIALS RESEARCH LABORATORY

NAME	*TITLE*
L. Simpson	Senior Research Associate
R. C. Abeyaratne	Research Associate
H. Araki	Research Associate
E. Berkcan	Research Associate
R. D. Kenway	Research Associate
H. Kwun	Research Associate

List of Staff in the Materials Research Laboratory Program

PHYSICS

NAME	TITLE
P. J. Bray	Professor
L. N Cooper	Professor
C. Elbaum	Professor (Applied Mathematics)
P. J. Estrup	Professor (Chemistry)
A. Houghton	Professor
H. Kolsky	Professor (Applied Mathematics) (Engineering)
H. J. Maris	Professor
J. J. Quinn	Professor
G. M. Seidel	Professor
P. J. Stiles	Professor
J. Tauc	Professor (Engineering)
S. C. Ying	Associate Professor
L. Friedman	Visiting Professor
K. H. Lau	Research Associate
K. P. Bohnen	Visiting Research Associate
G. Blanchet	Research Assistant
F. Bucholtz	Research Assistant
M. L. Buess	Research Assistant
J. Cameron	Research Assistant
M. C. Chang	Research Assistant
R. W. Cline	Research Assistant
W. J. Dell	Research Assistant
A. E. Geissburger	Research Assistant
S. G. Greenbaum	Research Assistant
D. Grempel	Research Assistant
M. D. Han	Research Assistant
I. A. Harris	Research Assistant
C. Huber	Research Assistant
T. E. Huber	Research Assistant
J. S. Kofol	Research Assistant
J. Lee	Research Assistant
M. Lega	Research Assistant
A. LeGrand	Research Assistant
M. Lui	Research Assistant
R. Mayer	Research Assistant
P. O'Connor	Research Assistant
G. Park	Research Assistant
B. Parker	Research Assistant
S. Ray	Research Assistant
G. Robertshaw	Research Assistant

S. Semancik	Research Assistant
M. Spitzer	Research Assistant
E. Vera	Research Assistant
K. C. Woo	Research Assistant
K. S. Yi	Research Assistant

Index, Principal Investigators

END

DATE
FILMED

11-81

DTIC